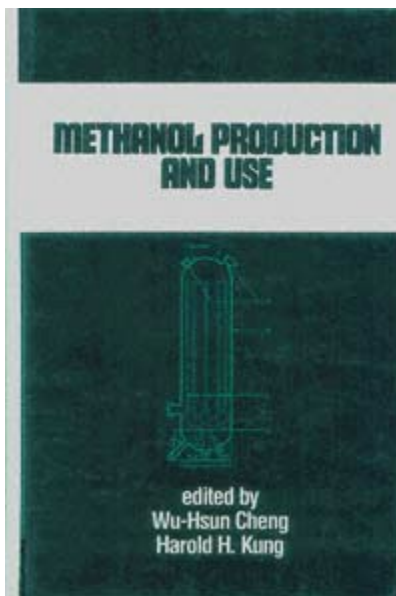


# METHANOL PRODUCTION AND USE



edited by  
**Wu-Hsun Cheng**  
**Harold H. Kung**



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# Methanol Production and Use

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# Methanol Production and Use

Edited by  
Wu-Hsun Cheng  
Chang Gung College of Medicine and Technology  
Taiwan, Republic of China

Harold H. Kung  
Northwestern University  
Evanston, Illinois

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## Preface

Methanol is perhaps the simplest organic molecule that can be used as a building block for larger, more complicated organic molecules. For many years, technology has been developed to produce methanol from various sources, the most recent being from conversion of natural gas or coal. Traditionally, the primary uses of methanol have been for chemical production, as either a feedstock or a solvent or cosolvent. In the late 1980s, the estimated consumption of methanol was about 15,000 metric tons per year. However, two recent developments could significantly change the demand for methanol. One is the requirement of oxygenates in transportation fuel. The potential of using methanol as fuel has led to the California Fuel Methanol Study by Bechtel, Inc., sponsored by various industries. Their report, issued in January 1989, stated that, although substantial use of methanol as fuel is unlikely in the immediate future, the required incorporation of oxygenates in gasoline has added a significant demand for methanol in the form of ethers, particularly methyl tert-butyl ether (MTBE).

The second development is the recent discovery that agricultural plants treated with methanol grow faster and bigger. Research is still going on to map out the exact conditions under which application of methanol is beneficial. This area provides another huge potential market for the compound.

The preparation of this book was conceived in late 1990 when one of us (W.-H. C.) was with the Central Research and Development Department of the DuPont Co., Wilmington, Delaware. At that time, the editors and Marcel Dekker, Inc., perceived a need for a comprehensive treatise on methanol that would cover the technical and business aspects of the compound. This book covers various topics to satisfy the needs of research managers, research and development scientists and engineers, and planning and design engineers interested in market analysis, safety in handling, chemical and physical properties, and technical aspects dealing with production and industrial uses of methanol. After the general introductory chapter, the book starts with a compilation of the properties of methanol. Then the technical aspects of production of methanol are described, which include discussions of the chemistry, engineering, and economics of the current production processes. This is followed by technical discussions of processes that use methanol, such as the processes to convert methanol to gasoline and olefins and the production of acetic acid, formaldehyde, acetaldehyde, ether, formate, and higher alcohols. The book then turns to the topic of large potential uses of methanol for transportation fuels and for agriculture. A description of applications not covered follows. The book ends with a chapter on the global picture of supply, demand, and marketing of methanol.

The book is written for readers with a general technical background. In the discussion of the future of methanol, technical objectivity was encouraged. We hope that this has been accomplished. The completion of this book would not have been possible without assistance from a large number of people. Most important are the contributors, who prepared their work in a timely and professional manner. Special thanks are given to Dr. Glyn Short of ICI-America for suggesting various contributors for this project. Thanks should also be given to the publishers and authors who granted us permission to use their figures.

WU-HSUN CHENG  
HAROLD H. KUNG

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## Contributors

Andrew A. Benson

Marine Biology Research Division, Scripps Institution of Oceanography, La Jolla, California

Chauchyun Chang

Union Chemical Laboratories/Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China

Clarence D. Chang

Central Research Division, Mobil Research and Development Corporation, Princeton, New Jersey

Wu-Hsun Cheng

Department of Chemical Engineering, Chang Gung College of Medicine and Technology, Kweishan, Taoyuan, Taiwan, Republic of China

James R. Crocco

Crocco & Associates, Inc., Houston, Texas

Harold H. Kung

Department of Chemical Engineering, McCormick School of Engineering and Applied Sciences, Northwestern University, Evanston, Illinois

J. R. LeBlanc

Fertilizers and Synthesis Gas Based Chemicals, The M. W. Kellogg Company, Houston, Texas

Deepak Nair  
Methanex Inc., Houston, Texas

Arthur M. Nonomura  
Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, Arizona

Robert V. Schneider, III  
Fertilizers and Synthesis Gas Based Chemicals, The M. W. Kellogg Company, Houston, Texas

Glyn D. Short  
ICI Americas, Wilmington, Delaware

Kevin J. Smith  
Department of Chemical Engineering, University of British Columbia, Vancouver, British Columbia, Canada

Richard B. Strait  
Fertilizers and Synthesis Gas Based Chemicals, The M. W. Kellogg Company, Houston, Texas

Barry L. Yang  
Department of Chemical Engineering, Northwestern University, Evanston, Illinois

## 1

## Overview

Wu-Hsun Cheng

Chang Gung College of Medicine and Technology, Kweishan, Taoyuan, Taiwan, Republic of China

Harold H. Kung

Northwestern University, Evanston, Illinois

## 1.1

## Introduction

Methanol is one of the largest volume commodity chemicals produced in the world. World methanol capacity has grown from 15.9 million t in 1983 to 22.1 million t in January 1991. Methanol consumption is increasing at a rate of about 11% per year during 1990-1995 [1]. This is largely attributed to increasing demand for methyl tert-butyl ether (MTBE), which is one of the fastest growing chemicals in the world.

Methanol has drawn keen attention a number of times in the chemical and energy industry. It plays an important role in C<sub>1</sub> chemistry. It is also regarded as one of the most promising alternative automobile fuel not based on petroleum.

This chapter briefly describes the historical development of methanol-related events and technologies and gives an overview of state-of-the-art methanol production technologies, the reactions and applications of methanol, and future opportunities.

## 1.2

## Historical Development of Methanol

Table 1 summarizes the historical development of methanol-related events and technologies. Methanol was first commercially produced by destructive distil-

Table 1 Historical Development of Methanol

Year	Events
1830	First commercial methanol process by destructive distillation of wood
1905	Synthetic methanol route suggested by French chemist Paul Sabatier
1923	First synthetic methanol plant commercialized by BASF
1927	Synthetic methanol process introduced in United States
Late 1940s	Conversion from water gas to natural gas as source of synthetic gas for feed to methanol reactors
1966	Low-pressure methanol process announced by ICI
1970	Acetic acid process by methanol carbonylation introduced by Monsanto
1973	Arab oil embargo reassessment of alternative fuels
1970s	Methanol-to-gasoline process introduced by Mobil
1989	Clean air regulations proposed by Bush administration
1990	Passage of the amended Clean Air Act in United States
Early 1990s	Discovery of enhanced crop yields with methanol treatment

lation of wood in 1830. This process prevailed for about a century until the first synthetic methanol plant was introduced by Badische Anilin-und-Soda-Fabrik (BASF) in 1923. DuPont introduced the synthetic methanol plant in the United States in 1927. In late 1940, natural gas replaced water gas as a source of syngas (i.e., CO and H<sub>2</sub>). ICI announced a low-pressure methanol process in 1966 using a copper-based catalyst. This operates at 510 MPa (50100 atm) compared with 35 MPa (35 atm) for the older high-pressure process. The Arab oil embargo in 1973 first generated much interest in methanol as an alternative automobile fuel. In 1989, the Bush administration proposed clean air regulations that would mandate the use of cleaner alternative automobile fuels. Methanol was favored by the administration. The amended Clean Air Act, passed in 1990, requires a reduction in ozone and carbon monoxide emissions, although it does not mandate use of an alternative fuel. The first phase of the amended act requires that gasoline marketed in 41 CO nonattainment areas must contain 2.7 wt% oxygen during the November-February control season starting 1992. In addition, ozone nonattainment areas will require the use of reformulated gasoline containing 2 wt% oxygen by January 1, 1995 [2]. Currently, methyl tert-butyl ether derived from isobutene and methanol is the most widely used oxygenate in reformulated gasoline, and automakers and local government authorities have announced plans to introduce methanol-fueled vehicles [36]. Thus, interest in methanol in fuel applications has shifted from economic considerations in the 1970s to environmental considerations in the 1990s. This environmental impact will continue into the next century and could have a strong effect on the demand for methanol. Furthermore, it was recently discovered that some crops

treated with methanol or nutrient-supplemented methanol showed significant increases in crop yields [7]. This has opened up another area of research and development for methanol and provides another opportunity for future methanol growth.

### 1.3

#### Production of Methanol

Methanol can be produced from a variety of sources, such as natural gas, coal, biomass, and petroleum. Table 2 summarizes the various processes, feedstocks, and catalysts.

Table 2 Feedstocks, Processes, and Catalysts for Production of Syngas and Methanol

Feedstocks	Processes and main reactions	Catalysts
Formation of syngas		
Natural gas	Steam reforming: $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	Ni on $\text{Al}_2\text{O}_3$
Natural gas	Autothermal reforming: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ , then $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$ , $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	— Ni on refractory supports
Natural gas	Partial oxidation: $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	Noncatalytic or lanthanide/Ru, supported Ru, Ni, Pd
Coal	Gasification (in presence of $\text{H}_2\text{O}/\text{O}_2$ )	—
Biomass	Gasification	—
Others (e.g., liquefied petroleum gas, naphtha, heavy fuel oil)	Steam reforming (light hydrocarbons)	Alkalized Ni on $\text{Al}_2\text{O}_3$ or on $\text{Ca}/\text{Al}_2\text{O}_3$
Formation of methanol		
Syngas	Methanol synthesis: $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ , $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	Cu/ZnO/ $\text{Al}_2\text{O}_3$ , Cu/ZnO/ $\text{Cr}_2\text{O}_3$ , or Zn/Cr
Syngas	Two-step methanol synthesis: $\text{CH}_3\text{OH} + \text{CO} \rightleftharpoons \text{HCOOCH}_3$ , then $\text{HCOOCH}_3 + 2\text{H}_2 \rightleftharpoons 2\text{CH}_3\text{OH}$	Potassium methoxide, Cu chromite
Methane	Direct oxidation: $\text{CH}_4 + \frac{1}{2}\text{O}_2$ (or $\text{N}_2\text{O}$ ) $\rightleftharpoons \text{CH}_3\text{OH}$	Metal oxides (e.g., $\text{MoO}_3$ based)
Methane	Bioprocessing	Enzymes (e.g., cytochrome $\text{P}_{450}$ ), methanotrophs



and catalysts for the production of methanol and its precursor, syngas. Methanol is synthesized industrially via syngas. Alternative processes considered but not commercialized include synthesis from syngas in two steps via methyl formate [8], direct oxidation of methane over a heterogeneous catalyst, and bioprocessing [9].

Natural gas will continue to be an important source of energy and chemical feedstocks. However, much of the natural gas reserve is situated in remote locations. Liquefying natural gas for shipping requires huge capital investment at the source and expensive, specially constructed transport fleets and receiving terminals. The evaporative loss of cryogenic LNG (liquified natural gas) must be controlled. Conversion of natural gas to methanol appears to be one of the most promising alternatives in utilizing abundant remote natural gas. This can be accomplished by direct and indirect routes.

### 1.3.1

#### Indirect Route via Syngas

The conversion of natural gas to methanol via syngas is a widely used industrial process. A typical conventional process includes desulfurization of natural gas, steam reforming, methanol synthesis and purification by distillation. Steam reforming of natural gas is an endothermic reaction and operates at high temperatures (reformed gas effluent at about 800–880°C). Methanol synthesis from syngas is an exothermic reaction and operates at 200–300°C. Heat integration and recovery is an important feature of the process. The trend in methanol production has been toward larger capacity and improved energy efficiency.

Production of syngas is traditionally performed in one step by steam reforming. Many of the modern processes adopt two-step reforming: primary steam reforming followed by autothermal reforming (Table 2). The primary reformer is simplified and reduced in size and can be operated at a reduced temperature. Oxygen is blown to the autothermal reformer first to produce CO and H<sub>2</sub>O with heat generation. The secondary reforming operates at higher temperatures to ensure low leakage of methane. The combined process is integrated to produce stoichiometric syngas for methanol synthesis. The process reduces energy consumption and investment and is particularly suitable for larger capacities. The two-step reforming process has been used by Topsøe, Lurgi, Mitsubishi, and others.

Syngas can also be produced by partial oxidation of methane. It is a mildly exothermic and selective process. It yields an H<sub>2</sub>/CO ratio lower than that by steam reforming. Traditionally, it operates at very high temperatures. Catalytic partial oxidation holds promise to reduce the operation temperature drastically. This could be an ideal process for the production of methanol syngas.

Methanol synthesis is another important step in the integrated process. Current low-pressure processes operate at 510 MPa (50100 atm) in vapor phase using quench (ICI), tubular (Lurgi), or double-tube heat-exchange (Mitsubishi) reactors. Single-pass conversion of syngas is low and is limited by equilibrium conversion. A high rate of gas recycling is needed. Cu/ZnO-based catalysts are industrial low-pressure methanol synthesis catalysts. In general, the selectivity of the catalysts decreases when operating at high pressures, high temperatures, high CO/H<sub>2</sub> or CO/CO<sub>2</sub> ratios, and low space velocities [10]. Improved catalyst activity would allow a change in operation conditions in favor of high selectivity. Fundamental studies on reaction mechanisms and kinetics, active sites, and effects of process conditions have been the subject of many research programs and have been discussed in several review papers [1113]. New types of effective catalysts and reactors are receiving significant attention.

## Catalysts

Recent advancements in catalyst development have led to some promising catalysts not based on Cu/ZnO. These may be classified into five types: intermetallic Cu/Th, Cu/lanthanides, Pt group on silica, Raney Cu, and homogeneous catalysts. It should be pointed out here that some of these potential catalysts are active at 100°C or lower. This would permit high conversions of syngas in a single pass and therefore reduce or eliminate costly gas recycling. For example, an ICI group has shown that Cu/lanthanides catalysts, when properly treated, can be active at temperatures as low as 70°C [14]. Brookhaven National Laboratory has developed a liquid-phase system that would permit the reaction to proceed at fully isothermal conditions around 100°C [15].

Even the industrial copper/zinc/alumina-based catalysts have been modified to achieve higher productivity or longer catalyst life. ICI recently announced its third-generation copper/zinc/alumina catalyst, described as a "step change" over the previous catalysts [16, 17]. This development was made through optimized formulation and particle and pellet size. Researchers at the University of New South Wales, Australia claimed another new breakthrough on this type of the catalyst [16]. A 100% improvement in performance over the previous catalysts was claimed.

## Reactors

In parallel with the development of high-activity catalysts, researchers are studying other types of reactors that would prevent the hot-spot phenomenon associated with the current fixed-bed reactor and/or increase the single-pass conversion. These include fluidized-bed, recirculating fluidized-bed, slurry, trickle-bed, gas-solid-solid trickle-flow, and liquid-phase reactors. Complete single-pass conversion has been demonstrated using continuous methanol removal by liquid or solid absorbents [18,19].

### 1.3.2

#### Direct Oxidation

In the past few years, there have been many active research programs around the world on the direct conversion of methane to methanol and/or formaldehyde, C<sub>2</sub> hydrocarbons, and others. Methanol and formaldehyde can be produced by partial oxidation of methane under controlled conditions in a homogeneous or catalytic reaction process. Many catalysts, such as Mo-based oxides, aluminosilicates, promoted superacids, and silicoferrate, have been used for the reaction. Since the activation energy for the subsequent oxidation of methanol and formaldehyde to carbon oxides is usually smaller than that for partial oxidation, high selectivities for methanol and formaldehyde have been demonstrated only at low methane conversions. Reaction conditions (e.g., O<sub>2</sub> or N<sub>2</sub>O to CH<sub>4</sub> ratio, temperature, and residence time) and surface area of supports play important roles in methanol and formaldehyde yield. In general, low pressure favors the formation of formaldehyde. High pressure and low O<sub>2</sub>/methane ratios favor the formation of methanol. The low yields achieved to date are a major obstacle to economical commercialization of this route.

### 1.3.3

#### Economics

Conversion of remote natural gas to methanol even by conventional methanol technology is economically competitive compared with shipping LNG. Delivered fuel cost based on a 323 billion Btu/day project and 6800 mile shipping distance was estimated to be about \$4.6/million Btu (calculation of capital was based on U.S. Gulf Coast, 1986) using conventional methanol technology and about \$4.8/million Btu for LNG [15]. Advanced and potential methanol technologies would make the methanol route even more attractive. Delivered fuel cost based on Brookhaven's low-temperature methanol process was claimed to be only \$3.6/million Btu under the same conditions [15]. The capital cost for production facilities, shipping tankers, and receiving terminals would be about 50% lower than the LNG investment.

Economics of the methanol technologies for remote natural gas has also been studied by Catalytica [20]. They described improved methanol technologies, such as advanced syngas generation using oxygen followed by improved ICI technology or including, CO<sub>2</sub>/H<sub>2</sub>O removal in the syngas production step, followed by low-temperature methanol synthesis. These improved technologies have a \$0.060.08/gal advantage over conventional methanol technology. Additional several cents/gal savings can be realized if a high-yield process of direct oxidation of methane to methanol can be successfully developed.

Methanol production is the most profitable way to add values to natural gas [21]. Methanol production is shifting from developed countries to developing



countries. New plants will be located in increasingly varied and remote locations to utilize abundant remote natural gas.

## 1.4 Reactions and Applications of Methanol

Methanol has been used in a variety of applications, which can be divided into three categories: feedstock for other chemicals, fuel use, and other direct uses as a solvent, antifreeze, inhibitor, or substrate. Primary and secondary derivatives or applications of methanol are summarized in Table 3. Chemical feedstock accounted for 62% of the total U.S. methanol consumption of 5.16 million t in 1990; fuel use for 27%, and other direct uses for 11% [1]. Growth in methanol consumption in the next few years will come largely from fuel use, especially MTBE [22, 23]. The demand pattern will change. SRI (Stanford Research Institute) International forecasted that the fuel industry will become the largest sector for U.S. methanol consumption in 1995. It will account for 54% of about 8.6 million ton methanol demand, followed by 39% as a chemical feedstock and 7% in other uses [1].

### 1.4.1 Reactions

Methanol is the simplest aliphatic alcohol. It contains only one carbon atom. Unlike higher alcohols, it cannot form an olefin through dehydration. However, it can undergo other typical reactions of aliphatic alcohols involving cleavage of a C-H bond or O-H bond and displacement of the -OH group [24]. Table 4 summarizes the reactions of methanol, which are classified in terms of their mechanisms. Examples of the reactions and products are given.

Homolytic dissociation energies of the C-O and O-H bonds in methanol are relatively high. Catalysts are often used to activate the bonds and to increase the selectivity to desired products.

### 1.4.2 Applications in the Energy Industry

Applications of methanol in the energy industry may be via four approaches: methanol-to-gasoline conversion, methanol to MTBE for reformulated gasoline, neat methanol or methanol blends as automobile and other fuels, and dissociation or reforming of methanol to syngas or H<sub>2</sub> for a variety of fuel uses. The need for these approaches is progressive. Mobil's methanol-to-gasoline process received wide interest in the 1970s and early 1980s, when the price of crude oil was high. MTBE and other ether additives in gasoline, such as ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME), are octane enhancers and are being used in reformulated gasoline for reducing automobile emissions. Methanol is one of the most promising alternative automobile fuels from a



Table 3 Overview of Methanol Applications

Direct derivatives or uses	Secondary derivatives or uses
Fuel or fuel additives	
Neat methanol fuel	
Methanol blended with gasoline	
MTBE	Oxygenate in gasoline
TAME	Oxygenate in gasoline
Methanol to gasoline	
Chemicals	
Formaldehyde	Urea-formaldehyde resins
	Phenolic resins
	Acetylenic chemicals
	Polyacetal resins
	Methyl diisocyanate
Acetic acid	Vinyl acetate
	Acetic anhydride
	Ethyl acetate
	Solvent for terephthalic acid
Chloromethanes	
Methyl chloride	Organic paint-removal solvent
Methylene chloride	Solvent and cleaning application
	Auxiliary blowing agent
Chloroform	HCFC-22 as a refrigerant
Methyl methacrylate	Acrylic sheet
	Molding and extruding compounds
	Coating resins
	Polyester
Dimethyl terephthalate	
Methylamines	
Monomethylamine	n-Methyl-2-pyrrolidone, water-gel explosives
Dimethylamine	Dimethylformamide, dimethylacetamide
Trimethylamine	Choline chloride
Glycol methyl ethers	
Ethylene oxide based	Solvents for paints, varnishes
Propylene oxide based	Solvents for paints, coatings, ink
Miscellaneous chemicals, such as dimethylphthalate, methyl acrylate, methyl formate, sodium methylate, nitroanisole, dimethylaniline	
Other uses	
Solvent	
Windshield solvent	
Process solvent	
Antifreeze	
Cooling agent in vehicles	
Inhibitor	

Hydrate inhibitor in natural gas processing

Inhibitor for formaldehyde polymerization

Substrate

Single-cell protein (animal feed substitute or nutritional source for human food)

Crop growth

Sewage treatment



Table 4 Reactivities of Methanol

Mechanism	Reactions	Other reactants	Product
O-H bond cleavage	Esterification	Acetic acid	Methyl acetate
		Phosgene	Dimethyl carbonate
		Terephthalic acid	Dimethyl terephthalate
	Addition	Acetone	Ketal
Hydroxyl group displacement	Halogenation	Isobutene	Methyl t-butyl ether
		HCl	Methyl chloride
	Carbonylation	CO	Acetic acid
	Dehydration		Dimethyl ether
C-H bond and O-H bond cleavage	Ammonolysis	NH <sub>3</sub>	Methylamines
	Oxidative dehydrogenation	O <sub>2</sub>	Formaldehyde
	Dissociation		CO and H <sub>2</sub>

nonpetroleum source. Its acceptance must be progressive, starting from the most polluted areas. Advanced technology of dissociating methanol on-board a vehicle before being fed into the engine perhaps represents the ultimate method of using methanol as a clean and efficient fuel.

#### 1.4.2.1

##### Methanol to Gasoline

Researchers at Mobil discovered in the 1970s that methanol can be converted to gasoline selectively using the zeolite ZSM-5. Hydrocarbons of C<sub>5</sub>C<sub>10</sub> of gasoline range can be produced in high yields because of the shape selectivity of the zeolite catalyst. The catalyst and the reaction process have been the subject of many studies and reviews. A large-scale plant has been constructed in New Zealand based on methanol from natural gas. Although the economics of the process is not competitive at current crude oil prices and no other commercial plants are planned, the process is the most remarkable technological advancement in synthetic petroleum since the Fischer-Tropsch process.

#### 1.4.2.2

##### Methyl tert-Butyl Ether

MTBE, produced by reacting methanol with isobutene, is entering a fast growth period. It has been used as an octane booster in gasoline. The properties of MTBE and other fuel oxygenates are described in Table 5. With the introduction of the amended Clean Air Act in the United States, oil companies are introducing cleaner automobile fuels to reduce ozone and smog in the most pol-

Table 5 Properties of Fuel Oxygenates

	Gasoline	Methanol	Ethanol	MTBE	ETBE	TAME
Blending octane, $1/2(\text{RON} + \text{MON})$	87	101	101	108	111	102
Heat of combustion, 103 Btu/gal	124.8	64.5	76.5	108.5	116.5	111.9
Boiling point, °C	Range	64.6	78.5	55.4	72.8	86.3
Specific gravity	0.74	0.79	0.79	0.75	0.74	0.77

RON: Research Octane Number.

MON: Motor Octane Number.

luted cities. The use of low-emission reformulated gasoline is a very cost-effective method and is favored by oil companies.

High concentrations of light olefins and aromatics in gasoline are unacceptable because of environmental concerns. Light olefins have a high blending vapor pressure and high atmospheric reactivity that contribute to high ozone formation. It has also been shown that reducing the concentration of aromatics in gasoline reduces the amount of  $\text{NO}_x$ , CO, and hydrocarbon emissions [25]. The Clean Air Act will limit the aromatic content in reformulated gasoline to 25% maximum [2]. Thus, clean-burning substitutes for volatile olefins and aromatics in gasoline are needed. Oxygenates in gasoline reduce CO and hydrocarbon emission because of the oxygen content. For example, unleaded gasoline containing 2 wt% oxygen on average reduces hydrocarbon emission by about 10%, and CO emission is reduced by about 17% compared with no-oxygen fuels [25]. MTBE, the best known fuel ether, can be produced at a reasonable cost and investment. Its use requires no changes in current automobiles or fuel distribution systems. It has high octane rating and is a key additive in reformulated gasoline.

### 1.4.2.3

#### Methanol and Methanol Blends

Methanol and methanol blends, such as M85 (85% methanol and 15% gasoline), are good fuels for spark-ignited internal-combustion engines. A study by the Los Alamos National Laboratory on the market penetration in 2025 of various alternative-fuel passenger vehicles concluded that internal-combustion vehicles powered by methanol are the most viable alternative to gasoline among 10 options studied [26]. Methanol may also be used as a fuel for turbines and methanol fuel cells. Its use as an alternative automobile fuel has received wide attention and was discussed considering environment, technology, economy, and energy security factors [27].

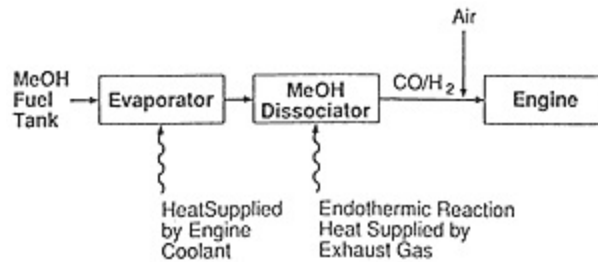


Figure 1

Use of methanol dissociator in an automobile.

#### 1.4.2.4

#### Dissociated Methanol

Although undissociated liquid methanol is a promising automobile fuel, dissociation of methanol to CO and H<sub>2</sub> on board a vehicle (Fig. 1) provides a fuel that is more efficient and cleaner than liquid methanol. Methanol dissociation is an endothermic reaction. The reaction heat can be provided by the engine exhaust gas. This recovers the waste heat and increases the heating value of the fuel. Internal-combustion engines running on dissociated methanol can be operated under leaner combustion than those on liquid methanol or gasoline and at higher compression ratios than those on gasoline. These further increase the thermal efficiency of the dissociated methanol fuel. Table 6 summarizes the contribution of these factors on thermal efficiency gain. Dissociated methanol could be up to 60% more efficient than gasoline and up to 34% better than undissociated methanol.

Table 6 Factors Contributing to Thermal Efficiency Gain for Dissociated Methanol

	% Increase in relative thermal efficiency	
	Over gasoline	Over undissociated methanol
Heat recovery in vaporizer	6	
Heat recovery in dissociator	14	14
High compression	10	
Lean combustion	30a	20a
Total	Up to 60	Up to 34

a Depending on engine load.

Source: communication with H. Yoon.

The dissociated methanol fuel that is rich in hydrogen and CO would be much cleaner than the liquid methanol fuel. Lean and complete combustion would ensure low CO and hydrocarbon emission. The formaldehyde emission would be improved. NO<sub>x</sub> emission would be greatly reduced because of lower combustion temperatures.

Experimental vehicles running on dissociated methanol have been operated by a number of organizations to demonstrate the feasibility and advantages of using dissociated methanol. Although the integrated methanol dissociation and engine systems have not been optimized, advantages have been clearly demonstrated. For example, Karpuk and coworkers modified a Ford Escort and showed that at a light engine load, dissociated methanol provided 17.7% lower fuel consumption and an order of magnitude reduction of NO<sub>x</sub> emission compared with lean-burning liquid methanol [28]. Lean combustion itself (say, at equivalence ratio of 0.3) has been shown to increase Otto cycle engine efficiency by up to 21% compared with nearly stoichiometric combustion [29]. Work at the Japan Automobile Research Institute also indicated high thermal efficiency and low exhaust emission levels during both transient and steady-state driving of a dissociated methanol-fueled car [30]. A number of patents and articles describe methanol dissociation catalysts, on-board reactors, and processes [3139].

### 1.4.3

#### Other Applications

Methanol as a chemical feedstock, a fuel, or a fuel additive covers most present methanol consumption. Other uses of methanol, although small for each, are broad. New uses of methanol are being explored and have potential for substantial growth. These other uses can be classified into four areas: solvent, antifreeze, inhibitor, and substrate.

#### 1.4.3.1

##### Solvent

Methanol is used as a solvent in automobile windshield washer fluid and as a cosolvent in various formulations for paint and varnish removers. It is also used as a process solvent in chemical processes for extraction, washing, crystallization, and precipitation. For example, methanol is used as an "antisolvent" for precipitation of polyphenylene oxide after its polymerization. It should be pointed out here that there have been active studies in using the extracts of agricultural plants in medicine. Methanol is often used for the extraction. Methanol extracts of some plants show antibacterial activities [4045]. This provides a potential use of methanol in traditional medicine.

#### 1.4.3.2

##### Antifreeze

Methanol has a high freezing point depression ability. It depresses the freezing point of water by 54.5°C for a 50/50 wt% methanol-water mixture [46]. The



largest antifreeze use of methanol is in the cooling system for internal combustion engines [47]. However, the antifreeze market for methanol has been saturated. Its market share has been lost to ethylene glycol since 1960 because of the superior performance of the glycol.

#### 1.4.3.3 Inhibitor

Methanol finds little use as an inhibitor. It inhibits formaldehyde polymerization and is present in the formaldehyde solution and paraformaldehyde. Methanol can also serve as a hydrate inhibitor for natural gas processing.

#### 1.4.3.4 Substrate

Methanol is an inexpensive source of carbon. It is a substrate used in many applications for supplying the energy needed for the growth of microorganisms. For example, single-cell protein, a protein in a variety of microbial cells, is produced through fermentation using hydrocarbon substrates, such as methanol [4850]. Methanol is also often chosen as the energy source for the microorganisms used in the biological nitrogen removal system for sewage treatment [5154].

### 1.5 Future Opportunities and Challenges

Recent forecasts on oxygenates and methanol all point to rapid increases in supply and demand [2123, 5456]. The Clean Air Act in the United States is a longterm commitment to air quality. Implementation of the second phase of the Clean Air Act will start in 1997 following the first phase in 1995. The oxygenate demand in the rest of the world is also increasing, largely driven by a need for octane enhancement when leaded gasoline is phased out. If these countries also adopt clean air regulations, a further substantial increase in oxygenate demand worldwide is foreseeable. Finland introduced a reformulated fuel in 1991 [57]. An analyst sees world oxygenate demand possibly growing more than 10-fold from 1992 to 2001 [54]. Crocco and Associates also anticipates that MTBE will continue to be the fastest growing petrochemical in the world, with methanol the second [21].

Besides fuel oxygenates, new uses are being studied, such as using methanol as an inexpensive carbon source to enhance crop growth [7] and for fermentation [58] and using dissociated methanol as a clean hydrogen fuel [27, 35]. These and the need to keep up with the demand for methanol and oxygenates provide ample opportunities and challenges for business and research and development.

#### 1.5.1 Production of Methanol

Global methanol demand will increase about 8%/year from 1991 to 1995 [21]. This increase in demand may be met by increasing nameplate capacity through

bottlenecking, conversion of ammonia plants to methanol, and adding small methanol plants in the United States and worldscale plants in remote locations. The M. W. Kellogg Company expects to see nine worldscale plants constructed in the period 1991-1996 [59]. Production of methanol is the most promising choice for moving low-cost remote natural gas to the marketplace.

Research and development to increase the efficiency of converting natural gas to methanol is challenging. Engineering and process improvements to reduce the energy demand per ton methanol and  $\text{NO}_x$  and  $\text{CO}_2$  emissions have been actively sought. Combined reforming and parallel reforming are alternatives to conventional steam reforming in the syngas production step [60, 61]. There are also many research opportunities in three important areas: catalytic partial oxidation of methane to syngas, the syngas-to-methanol process with high single-pass conversions, and direct oxidation of methane to methanol. Their successful development would drastically improve the economics of methanol production.

The partial oxidation reaction of methane to syngas is mildly exothermic, in contrast to highly endothermic steam reforming. It could produce stoichiometric syngas for methanol synthesis in one step. It is an ideal process for producing methanol syngas. Effective catalysts are needed to carry the reaction selectively at mild temperatures. A recent finding by researchers at the University of Oxford indicated that the reaction could be carried out selectively at  $775^\circ\text{C}$  (97+% selectivity at 94% conversion) using lanthanide ruthenium oxide or alumina-supported ruthenium catalysts, in contrast to more than  $1200^\circ\text{C}$  in conventional processes [62].

The equilibrium of the methanol synthesis reaction severely limits the conversion in the conventional process. The equilibrium conversion is very sensitive to temperature. The high recycling rate is costly and requires oxygen instead of air in the autothermal reforming or partial oxidation step. The development of low-temperature and continuous methanol removal processes mentioned briefly in Section 1.3.1, would be very attractive [63-65]. High single-pass conversion could also be attained with a two-step process: methanol carbonylation to methyl formate followed by methyl formate hydrogenolysis to 2 mol methanol [66-69]. Research in these areas has yielded promising results.

The direct oxidation of methane to methanol has shown only limited success. The process would be very economical if it could achieve 80% selectivity at 80% conversion, based on Catalytica's evaluation. The development of selective catalysts and effective reaction processes is challenging. Bioprocessing that has potential for high selectivity is also worth further research.

## 1.5.2 Methanol Use

Many technically challenging opportunities exist in the improvement of current processes or development of new processes for the present use of methanol and





in developing new uses. Many of these would lead to new business or improve the quality and quantity of existing business because of better economics, improved environmental compatibility, or better feedstock position.

### 1.5.2.1

#### Present Use

Methanol plays a central role in C<sub>1</sub> chemistry. Research on the reactions of methanol continues to be very active. For example, the carbonylation of methanol to acetic acid using the Rh complex catalyst and the iodide promoter has some drawbacks, although it was an important achievement. Successful development of a noniodide system would eliminate the corrosion problem and the need for using expensive zirconia as a material of construction. There is also active research on nonRh-based catalysts [70] and polymer-supported Rh catalysts [71]. SRI International reported that the latter could be more economical than the present homogeneous catalysis process [72].

MTBE is produced by reacting methanol with isobutene. Isobutene is contained in the C<sub>4</sub> stream from steam crackers and from fluid catalytic cracking in the crude oil-refining process. However, isobutene has been in short supply in many locations. The use of raw materials other than isobutene for MTBE production has been actively sought. Figure 2 describes the reaction network for MTBE production. Isobutene can be made by dehydration of t-butyl alcohol, isomerization of n-butenes [73], and isomerization and dehydrogenation of n-butane [74, 75]. t-Butanol can also react with methanol to form MTBE over acid alumina, silica, clay, or zeolite in one step [7678]. t-Butanol is readily available by oxidation of isobutane or, in the future, from syngas. The C<sub>4</sub> fraction from the methanol-to-olefins process may be used for MTBE production, and the C<sub>5</sub> fraction may be used to make TAME. It is also conceivable that these

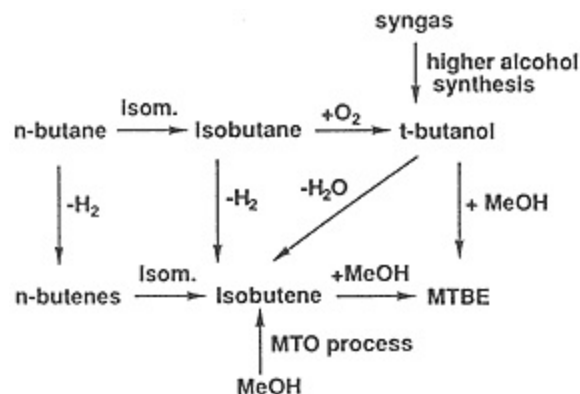


Figure 2  
Feedstocks and reaction network for MTBE production.  
(From Ref. 27.)

ethers could be based on nonpetroleum sources. These present vast research opportunities for developing efficient catalysts and integrated processes depend on the availability of feedstocks. Reactive distillation, in which the reaction of isobutene and methanol and the distillation to remove MTBE occur in the same tower, is another active research area. Development of efficient processes to separate and recover unreacted methanol from C<sub>4</sub> at a low cost is being sought. Potential processes include using a light hydrocarbon stripping gas [79], silica as an absorbent [80], and pervaporation [81].

### 1.5.2.2

#### New Uses

##### Dissociated Methanol

Some applications of dissociated methanol are emerging:

- Alternative automobile fuel
- Supplemental gas turbine fuel at peak demand of electricity
- Supplying H<sub>2</sub> for fuel cells
- Fuel and cooling system for hypersonic jets
- Source of CO and H<sub>2</sub> for chemical processes and material processing

Dissociated methanol as an alternative automobile fuel was mentioned earlier (Sect. 1.4.2). Because of limited space in the engine compartment and limited temperatures during cold start, on-board methanol dissociation would need catalysts that are active at low temperatures. The activity and stability are two key points for these catalysts. Coke formation has been a problem that results in catalyst deactivation [82]. Methanol dissociation on board a vehicle also requires a compact and efficient heat-exchange reactor to make use of engine waste heat. The reactor should also be resistant to the maximum anticipated exhaust temperature, thermal cycling fatigue, hydrogen embrittlement, and methanol corrosion. Although a number of catalysts and dissociators have been devised [3139], there are still many opportunities for improvement.

Methanol dissociation on board a passenger vehicle operates near atmospheric pressure, a condition that thermodynamically strongly favors the dissociation reaction. However, applying the dissociation to a diesel engine would require operation at such high pressures as 1020 MPa (100200 atm). Exhaust gas temperatures from a diesel engine could vary in a wide range from as low as 150°C to well over 500°C. Development of an active and stable catalyst and technology to accommodate these harsh conditions is needed to use dissociated methanol for the diesel engine.

Methanol dissociation can also be driven by heat from gas turbine exhaust gas. This would increase the heating value and make dissociated methanol an

attractive peaking fuel for power plants. For this application, methanol dissociation must be conducted at about 1.52 MPa (1520 atm).

The dissociation of methanol could provide a convenient, economical, and clean source of CO and H<sub>2</sub> for applications in fuel cells, chemical processes (e.g., carbonylation, hydrogenation, and hydroformylation), and materials processing. As an on-site source of CO and H<sub>2</sub>, it can be operated under mild conditions and produces no sulfur or soot, as opposed to high-temperature reforming or partial oxidation using other hydrocarbons.

Because of its endothermic nature, methanol dissociation could provide not only an efficient fuel but also an effective method for cooling. For example, engine cooling is a critical issue for hypersonic jets being developed by the U.S. Air Force. Methanol dissociation is promising for both the cooling and fuel systems.

### Source of Carbon

#### Enhanced crop yield

It was found recently that treatment of some agricultural crops (e.g., C<sub>3</sub> crop plants) with methanol or nutrient-supplemented methanol under direct sunlight drastically increased turgidity [7]. The treatment stimulated growth rather than merely supported normal growth. This effect far exceeded that expected of a nutrient. However, in the shade or when other crops (e.g., plants with C<sub>4</sub> metabolism) were treated with methanol, they showed no growth improvement. This is an interesting finding. More studies are needed to understand the role of methanol and its applicability.

#### Wastewater treatment

In Sweden, many advanced sewage treatment plants for phosphorous removal and lowering of biological oxygen demand must be extended to nitrogen removal: a new policy in 1988 required 50% nitrogen removal for about 70 wastewater treatment plants. Organic matter in the wastewater has been a limiting factor for nitrogen removal in many cases. The addition of an external carbon source can be a cost-effective solution. Use of methanol as a carbon source has been tested in full scale at the Klagshamn plant and has shown promising results [83].

#### Inexpensive substrate in microbial production

Cheap methanol may be used as a carbon source to replace carbohydrate in the microbial production of chemicals. For example, polyhydroxybutyrate (PHB), a biodegradable thermoplastic material, can be produced by microbial fermentation. However, its high cost restricts large-scale application. The cost of the substrate is an important contributing factor to the overall cost of production. The use of methanol to produce PHB, if successfully developed without sacrificing the molecular weight, would significantly improve process economics and increase its practical application. Recent studies have shown promising results [58, 84, 85].



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## 2

## Physical and Chemical Properties and Handling Aspects

Barry L. Yang

Northwestern University, Evanston, Illinois

## 2.1

## Pure Methanol

Methanol is a clear, colorless, and volatile liquid, giving off a mild alcoholic odor at room temperature. It is polar, acid-base neutral, and generally considered non-corrosive. It is miscible with water and most organic solvents and is capable of dissolving many inorganic salts. Anhydrous methanol is hygroscopic. Methanol is toxic to human beings but is not considered particularly harmful to the environment.

Selected properties of pure methanol are given in Table 1. Two sets of values, one in SI units and the other in optional units, are given for the user's convenience. Table 1 is composed of data taken from References 16. A comprehensive data collection for a large number of organic solvents, including methanol, was made by Riddick et al. [2], and selected physical and thermodynamic properties of more than 700 aliphatic alcohols in the carbon range C<sub>1</sub>C<sub>50</sub> were evaluated by Wilhoit and Zwolinski [3]. Data screening and accuracy estimation were exercised by the authors of References 1 and 3. High-pressure data of viscosity and thermal conductivity of methanol have been given by Vargaftik [7]. Extended thermodynamic properties of methanol to 400°C and 70 MPa (690 atm) have been given by Goodwin [8], and that to 1500 K at 0.1 MPa (1 atm) have been given by Chao et al. [9]. Thermodynamic properties

Table 1 Basic Properties of Methanol

Property	SI value	Alternative value	ACa Reference	
Molecular weight	32.042 kg/kmol	32.042 g/mol	V	1
Liquid density (25°C, 1 atm)	786.4 kg/m <sup>3</sup>	0.7864 g/ml	B	2
Solid density (110°C)	980 kg/m <sup>3</sup>	0.980 g/ml	C	1
Melting point (MP)	175.47 K	97.68°C	C	1
Heat of fusion at MP	3.205 kJ/mol	23.91 cal/g	U	1
Triple-point temperature	175.6 K	97.6°C	B	1
Triple-point pressure	0.108 Pa	8.08 × 10 <sup>4</sup> torr	D	1
Boiling point (BP, 1 atm)	337.85 K	64.70°C	B	1
Heat of vaporization				
25°C	37.43 kJ/mol	0.2792 kcal/g	U	2
BP	35.28	0.2632	U	2
Critical temperature	512.6 K	239.4°C	B	1
Critical pressure	8.10 MPa	79.9 atm	C	1
Critical volume	0.118 m <sup>3</sup> /kmol	118 ml/mol	D	1
Critical density	272 kg/m <sup>3</sup>	0.272 g/ml	D	1
Critical compressibility factor	0.224		VU	1
Enthalpy of formation (25°C, 1 atm)				
Vapor	201.1 kJ/mol	48.06 kcal/mol	A	3
Liquid	239.0	57.13	A	3
Free energy of formation (25°C, 1 atm)				
Vapor	162.4 kJ/mol	38.82 kcal/mol	B	3
Liquid	166.8	39.87	B	3
Entropy (25°C, 1 atm)				
Vapor	239.7 J/mol/K	57.29 cal/mol/K	A	3
Liquid	127.2	30.41	A	3
Heat capacity				
Vapor (25°C, 1 atm)	43.89 J/mol/K	10.49 cal/mol/°C	A	3
Liquid (25°C, 1 atm)	81.17	19.40	A	3
Solid (97.6°C, 0.0011 torr)	49.25	11.77	A	3
Vapor pressure (25°C)	16.94 kPa	127.0 torr	B	2
Acentric factor	0.5656		VU	1
Radius of gyration	1.552 × 10 <sup>10</sup> m	0.1552 nm	VC	1
Solubility parameter	2.96 × 10 <sup>4</sup> J <sup>1/2</sup> /m <sup>3/2</sup>		VE	1
Van der Waals area	3.580 × 10 <sup>5</sup> m <sup>2</sup> /mol	0.594 nm <sup>2</sup> /molecule	VB	1
Van der Waals volume	2.171 × 10 <sup>5</sup> m <sup>3</sup> /mol	0.036 nm <sup>3</sup> /molecule	VB	1

(continued)

## Table 1 Continued

Table 1 Basic Properties of Methanol

Property	SI value	Alternative value	ACa Reference	
Dipole moment				
Vapor	$5.67 \times 10^{30}$ C-m	1.70 debye	B	1
Liquid (20°C)	$9.57 \times 10^{30}$	2.87	U	2
Surface tension in air (25°C)	0.0223 N/m	22.3 dyn/cm	C	2
Refractive index (25°C)	1.3265		A	1
Magnetic susceptibility (3°C)		$0.63 \times 10^6$ cgsm	U	4
Electrical conductivity (25°C)	$1.5 \times 10^7$ (ohm-m) <sup>1</sup>	$1.5 \times 10^9$ (ohm-cm) <sup>1</sup>	F	2
Dielectric constant (25°C)	32.66		U	2
Liquid thermal diffusivity (25°C)	$1.05 \times 10^7$ m <sup>2</sup> /s	$1.05 \times 10^3$ cm <sup>2</sup> /s	U	5
Thermal expansion coefficient (25°C)	0.001196 K <sup>-1</sup>	0.001196 °C <sup>-1</sup>	U	2
Viscosity (25°C)				
Vapor	0.00961 mPa-s	0.00961 cP	E	1
Liquid	0.549	0.549	E	1
Thermal conductivity (25°C)				
Vapor	0.0157 W/m/K	0.0000375 cal/s/cm/K	C	1
Liquid	0.203	0.000484	D	1
Flash point				
Open cup	289 K	16°C	U	6
Closed cup	284	11	U	1
Evaporation rate (n-butyl acetate = 1)	2.1		F	2
Autoignition temperature	737 K	464°C	U	1
	743	470	U	6
Explosive limits in air, vol%	7.336		U	1
	5.544		U	6
Heat of combustion (25°C, 1 atm)				
Vapor	764.1 kJ/mol	5.699 kcal/g	A	3
Liquid	726.1	5.416	A	3

a Accuracy code: A < 0.2% error, B < 1% error, C < 3% error, D < 5% error, E < 10% error, F > 100% error possible, U = unknown accuracy, V = value defined or calculated.

of deuterated methanols,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$ , have been reported by Chao et al. [9] and by Chen et al. [10].

Methanol in the solid phase has been discussed by Wilhoit and Zwolinski [3] and by Wilhoit et al. [11]. There are at least two crystalline forms of solid methanol. The low-temperature crystal II is orthorhombic, which transfers to crystal I at  $115.8^\circ\text{C}$  with an enthalpy change of  $0.636\text{ kJ/mol}$ . Crystal I is monoclinic. Its powder diffraction data have been collected in the JCPDS File [12]. Phase equilibria between solid and liquid and between liquid and vapor have also been discussed by Wilhoit and Zwolinski [3]. Phase equilibrium under pressure has been discussed by Goodwin [8]. Methanol vapor exhibits appreciable deviation from the ideal gas. The molecular association of methanol monomer into dimer and tetramer has been reported [3]. The equation of state and the difficulty associated with its determination have been discussed by Wilhoit and Zwolinski [3].

The temperature dependence of many properties of methanol has been described in figures, tables, and equations. Plots of vapor pressure, liquid density, liquid heat capacity, vapor heat capacity, heat of vaporization, surface tension, liquid thermal conductivity, vapor thermal conductivity, liquid viscosity, and vapor viscosity against temperature have been given by Yaws [13] and by Flick [14]. Tables of vapor pressure [3,15,17], liquid density [3,15,17], liquid volume [16], vapor density [15,17], vapor volume [16], liquid viscosity [15,18], vapor viscosity [15], surface tension [15,19], liquid heat capacity [15,17,20], vapor heat capacity [3,15,17], solid heat capacity [11], liquid thermal conductivity [15,17], vapor thermal conductivity [15], second virial coefficient [16], dielectric constant [21], refractive index [3], and heat of vaporization [16] have also been published. Thermodynamic properties of methanol in the condensed phases have been tabulated by Wilhoit et al. [11], and those in the gas phase have been given by Chao et al. [9].

Equations for the description of the temperature dependence of selected properties of methanol are given here, where  $T$  is temperature in K:

The vapor pressure  $P$  (Pa) of methanol in a limited temperature range can be described accurately by the Antoine equation [22]:

$$\log P = 10.20587 - \frac{1582.271}{T - 33.424}$$

$$288.0\text{ K} < T < 356.8\text{ K, error} < 0.06\%$$
(1)

For a wider range of temperature, Daubert and Danner [1] suggested the equation



$$\ln P = 109.93 - \frac{7471.3}{T} - 13.988 \ln T + 0.015281 T$$

$$175.6 \text{ K} < T < 512.6 \text{ K, error} < 1\% \quad (2)$$

For liquid density  $d$  (kg/m<sup>3</sup>), Daubert and Danner [1] suggested the equation

$$\ln d = 3.6541 + 1.62055 \left[ 1 + \left( 1 - \frac{T}{512.63} \right)^{0.17272} \right]$$

$$175.6 \text{ K} < T < 512.6 \text{ K, error} < 1\% \quad (3)$$

For more precise expressions, Wilhoit and Zwolinski [3] recommended the following:

$$d = 1100.98 - 0.9321T - \frac{423,280}{11,914 - T}$$

$$253 \text{ K} < T < 323 \text{ K, error} < 0.05\% \quad (4)$$

$$d = 1035.59 - 0.6111T - \frac{17,267}{556.23 - T}$$

$$313 \text{ K} < T < 453 \text{ K, error} < 0.1\% \quad (5)$$

Ideal gas heat capacity  $C_{p(g)}$  (J/mol/K) [1]:

$$C_{p(g)} = 38.188 + 104.24/e^{2186.7/T^{1.1628}}$$

$$100 \text{ K} < T < 1500 \text{ K, error} < 1\% \quad (6)$$

Liquid heat capacity  $C_{p(l)}$  (J/mol/K) [1]:

$$C_{p(l)} = 107.6 - 0.3806T + 0.000979T^2$$

$$175.6 \text{ K} < T < 400 \text{ K, error} < 1\% \quad (7)$$

Solid heat capacity  $C_{p(s)}$  (J/mol/K) [1]:

$$C_{p(s)} = -12.96 + 0.957T - 0.005002T^2 + 1.049 \times 10^{-5} T^3 + 7.1 \times 10^{-9} T^4$$

$$30 \text{ K} < T < 151 \text{ K, error} < 3\% \quad (8)$$

For vapor thermal conductivity  $k(g)$  (W/m/K), the equation recommended by Daubert and Danner [1] is

$$\ln k_{(g)} = 2.04937 + 1.0279 \ln T - \ln (7.436 \times 10^7/T - 6.77 \times 10^9/T^2 - 1)$$

$$273 \text{ K} < T < 684 \text{ K, error} < 3\% \quad (9)$$

For a wider range of temperature, Yaws [13] suggested

$$k_{(g)} = -7.7906 \times 10^{-3} + 4.1631 \times 10^{-5} T + 1.2134 \times 10^{-7} T^2 - 5.1798 \times 10^{-11} T^3$$

$$273 \text{ K} < T < 1273 \text{ K, accuracy not given} \quad (10)$$

Liquid thermal conductivity  $k_{(l)}$  (W/m/k) [1]:

$$k_{(l)} = 0.2872 - 0.0002838T$$

$$176 \text{ K} < T < 430 \text{ K, error} < 5\% \quad (11)$$

Vapor viscosity  $\eta_{(g)}$  (mPa-s) [1]

$$\log \eta_{(g)} = -3.51339 + 0.69655 \log T - \log \left[ 1 + \frac{205}{T} \right]$$

$$240 \text{ K} < T < 1000 \text{ K, error} < 10\% \quad (12)$$

For liquid viscosity  $\eta_{(l)}$  (mPa-s), the equation recommended by Viswanath and Natarajan [18] is

$$\log \eta_{(l)} = -1.9016 - \frac{449.49}{23.551 - T}$$

$$180 \text{ K} < T < 290 \text{ K, error} < 3\% \quad (13)$$

For higher temperatures, Daubert and Danner [1] recommended

$$\ln \eta_{(l)} = -0.3803 + \frac{1065.3}{T} - 0.6657 \ln T$$

$$230 \text{ K} < T < 375 \text{ K, error} < 10\% \quad (14)$$

Heat of vaporization  $\Delta H_v$  (kJ/mol) [1]:

$$\ln \Delta H_v = 3.68135 + (-0.279 + 9.9106 \times 10^{-4} T + 3.1971 \times 10^{-7} T^2) \ln \left[ 1 - \frac{T}{512.58} \right]$$

$$175.6 \text{ K} < T < 512.6 \text{ K, error} < 10\% \quad (15)$$

Surface tension  $\sigma$  (N/m) [1]:

$$\ln \sigma = 0.7676 \ln \left[ 1 - \frac{T}{512.58} \right] - 3.1403$$

$$176 \text{ K} < T < 512 \text{ K, error} < 3\% \quad (16)$$

The spectroscopic characteristics of methanol have been well documented. Molecular vibrational frequencies of CH<sub>3</sub>OH, CH<sub>3</sub>OD, CD<sub>3</sub>OH, and CD<sub>3</sub>OD

have been tabulated by Shimanouchi [23]. Characteristic vibrations for  $\text{CH}_3\text{OH}$  are at 3340, 2940, 2830, 1450, 1110, and 1030  $\text{cm}^{-1}$  [24]. Fourier-transform infrared (FT-IR) spectra of  $\text{CH}_3\text{OH}$  liquid,  $\text{CH}_3\text{OH}$  vapor (150°C), and  $\text{CD}_3\text{OD}$  liquid can be found in Reference 25. Raman data are in parallel with IR data [23,24]. The ultraviolet (UV) absorbance curve of methanol is smooth and featureless throughout the range 210–400 nm. Both  $^{13}\text{C}$  and  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra of  $\text{CH}_3\text{OH}$  can be found in Reference 26. Mass spectral data have also been collected [24,27]. Ionization energies and electron binding energies of methanol have been tabulated by Robinson [28].

## 2.2

### Methanol-Containing Systems

#### 2.2.1

##### Methanol-Water System

Properties including freezing point, boiling point, and flash point of methanol-water solutions of different methanol contents have been given by Flick [14]. Data for density [14,29], viscosity [14], vapor pressure [14,29], thermal conductivity [14], specific heat [14,29], surface tension [30], and refractive index [31] at selected temperatures have also been tabulated. Heat of mixing can be found in Reference 32. Diffusion coefficients of methanol and water in methanol-water solutions have been evaluated in detail by Derlacki et al. [33].

#### 2.2.2

##### Methanol-Organic Systems

A large collection of vapor-liquid equilibrium data for binary, ternary, and quaternary methanol-containing systems has been made by Gmehling and Onken [34]. A list of known azeotropes is given in Tables 2 and 3 [35]. Data for solubility [36,37], heat of mixing [32], and density [37] for selected systems are available. For methanol-hydrocarbon systems, data for heat of mixing [38] and excess volume [39] have been compiled. The solubility of methanol in gasoline can be found in Reference 14. A collection of diffusivities of various organic compounds in methanol is available [40]. Diffusivity and sorptivity of methanol through a polyurethane membrane have been reported [41].

#### 2.2.3

##### Methanol-Inorganic Systems

The capability of methanol in forming hydrogen bonds makes it a protic solvent, suitable for dissolving many inorganic compounds. Data for solubility [37,42–44], density [37], and heat of solution [32,44] of many electrolytes in methanol and deuterated methanol have been collected. Diffusivities of selected compounds in liquid methanol can be found in Reference 40. Solubilities of methanol in compressed gases of hydrogen, nitrogen, methane, and carbon



Table 2 Azeotropes of Methanol-Containing Binary Systems

Methanol (wt%)	Second component	Wt%	Boiling point (°C)
12	Acetone	78	55.7
19	Acetonitrile	81	63.45
6	Acetylene dichloride	94	27.5
61.3	Acrylonitrile	38.5	61.4
62	Allyl iodide	38	63.5
39.6	Benzene	60.4	58.34
40	Bromodichloromethane	60	63.8
11	2-Bromopropene	89	42.7
41.7	iso-Butyl bromide	58.3	61.25
24	tert-Butyl bromide	76	55.6
23	iso-Butyl chloride	77	53.05
27	n-Butyl chloride	73	57.0
10	tert-Butyl chloride	90	43.75
95	iso-Butyl formate	5	64.6
70	iso-Butyl iodide	30	60.0
98.8	Camphene	1.2	64.67
14	Carbon disulfide	86	37.65
20.56	Carbon tetrachloride	79.44	55.7
12.5	Chloroform	87.5	53.5
35	Chloromethyl methyl ether	65	56
3	2-Chloropropene	97	22.0
38.8	1,3-Cyclohexadiene	61.2	56.38
42.5	1,4-Cyclohexadiene	57.5	58
61	Cyclohexane	39	54.2
40	Cyclohexene	60	55.9
18	Cyclopentene	82	37
22.5	Diallyl	77.5	47.05
13	cis-Dichlorethylene	87	51.5
63	Diethyl sulfide	37	60.2
24.2	Dimethyl acetal	75.8	57.5
70	Dimethyl carbonate	30	62.7
60	2,5-Dimethyl hexane	40	61.0
15	Dimethyl sulfide	85	34
72	Di-n-propyl ether	28	63.8
44	Ethyl acetate	56	62.25
84.4	Ethyl acrylate	15.6	64.5
4.5	Ethyl bromide	95.5	34.95
32	Ethylene dichloride	68	69.95
16	Ethyl formate	84	50.95
82	Ethylidene bromide	18	64.2
11.5	Ethylidene chloride	88.5	49.05
18.5	Ethyl iodide	81.5	54.7
28	Ethyl n-propyl ether	72	55.8
32	Fluorobenzene	68	59.7

(table continued on next page)



## Table 2 Continued

Table 2 Azeotropes of Methanol-Containing Binary Systems

Methanol (wt%)	Second component	Wt%	Boiling point (°C)
51.5	n-Heptane	48.5	59.1
27	n-Hexane	73	49.5
26	n-Hexene	74	50
99.2	d-Limonene	0.8	64.63
19	Methyl acetate	81	54.0
54.0	Methyl acrylate	46.0	62.5
8.2	Methylal	91.8	41.85
50	Methyl-tert-amyl ether	50	62.3
10	3-Methyl 1,2-butadiene	90	35
3	3-Methyl butene-1	97	19.8
7	3-Methyl butene-2	93	31.75
75	Methyl iso-butyrate	25	64.0
15	Methyl tert-butyl ether	85	51.6
43	Methyl cyclohexane	57	59.45
8	Methylene dichloride	92	39.2
70	Methyl ethyl ketone	30	63.5
22.3	2-Methyl furan	77.7	51.5
4.75	Methyl n-propionate	95.25	62.45
10	Methyl n-propyl ether	90	38.85
91	Nitromethane	9	64.55
55	Nitroethane	45	61.82
72	n-Octane	28	63.0
4	iso-Pentane	96	24.5
9	n-Pentane	91	30.8
12	Pentene-2	88	31.5
90.7	$\alpha$ -Pinene	9.3	64.55
17	Piperylene	83	37.5
80	iso-Propyl acetate	20	64.5
15.0	iso-Propyl bromide	85.0	48.6
20.2	n-Propyl bromide	79.8	54.1
6	iso-Propyl chloride	94	33.4
9.5	n-Propyl chloride	90.5	40.5
53	Propylene dichloride	47	62.9
50.2	n-Propyl formate	49.8	61.9
21	Propylidene chloride	79	55.5
38	iso-Propyl iodide	62	61
61	n-Propyl iodide	39	63.5
63.5	Tetrachlorethylene	36.5	63.75
69	Toluene	31	63.82
97	1,1,2-Trichlorethane	3	64.5
36	Trichlorethylene	64	60.2
32	Trimethyl borate	68	54.6

Source: From Reference 35.

Table 3 Azeotropes of Methanol-Containing Ternary Systems

Methanol (wt%)	Second component	Wt%	Third component	Wt%	Boiling point (°C)
10	Ethyl bromide	50	Carbon disulfide	40	33.92
15	Ethyl bromide	55	2-Methyl butene-2	30	31.4
17.8	Methyl acetate	48.6	Cyclohexane	33.6	50.8
7	Methylal	38	Carbon disulfide	55	35.55

Source: From Reference 35.

dioxide at elevated pressures have been measured [45]. Data for mutual diffusivity of methanol vapor in air, hydrogen, and carbon dioxide at atmospheric pressure and a range of temperatures and that in nitrogen and in hydrogen at elevated pressures have been collected by Vargaftik [46].

## 2.2.4

### Adsorption of Methanol

The adsorption of methanol on the surface of a wide range of solid materials has been studied, with aimed applications in catalysis, electrochemistry, and processes utilizing adsorption-desorption. A list of selected literature reports is given in Tables 4 and 5, with each report addressed by its Chemical Abstract (CA) number. The materials studied include metals, oxides, and high surface area adsorbents, such as active carbon, silica gel, and zeolite. Adsorption on high surface area adsorbents is usually at ambient or mild temperatures and is often reversible. A compilation of selected adsorption equilibrium data has been made by Valenzuela and Myers [47]. Adsorption on metals and active oxides is often dissociative and accompanied by decomposition reactions. A review of the adsorption of methanol on eight transition metals and its characterization by electron spectroscopy has been given by Hegde [48]. Other techniques commonly used for the characterization of adsorbed methanol include infrared, nuclear magnetic resonance, temperature-programmed desorption, and calorimetry.

## 2.3

### Chemical Reactivity

#### 2.3.1

#### Industrially Important Reactions

Methanol shares chemical properties with other primary aliphatic alcohols, with most of its reactivity associated with the hydroxyl group. Many reactions of methanol involve the cleavage of either the C-OH bond or the O-H bond, leading to the substitution of the OH group or the proton. Methanol is an important chemical for the synthesis of a wide range of organic compounds. Table 6 lists



Table 4 Methanol Adsorption Literature: Vapor-Phase Adsorptiona

Solid surface	CA no. (year published)	Temperature (K)	Method
<b>Metalb</b>			
Pt(110)	114:23292h (1990)	1001000	TPD
Pt(111)	103:147692f (1985)	90350	IR, UPS
Pt black	75:10590e (1971)	290350	Isotherm, heat of adsorption
Rh(001), Rh(111)	112:157509b (1989)	298360	FIM, PFDMS
O-Rh(110)	116:6014t (1991)	315417	Isotope
Ru(110)	88:95218f (1977)	80	UPS
Pd(111), O/Pd(111)	99:175090a (1983)	140300	HREELS
Na/Pd(100)	105:232853v (1986)	120600	XPS, AES, LEED
Ag(111), O/Ag(111)	99:146687v (1983)	90400	XPS, UPS
Ni(110)	111:64642d (1989)	140450	TPD
Cu(110)	116:263011a (1992)	90300	TPD, IRAS
	113:103976d (1990)	90500	TPD, IRAS
Na/Cu(111), Na	103:184079g (1985)	100650	UPS, EELS
Cu-Pd, O-Cu-Pd	102:191812y (1985)	80220	UPS, EELS
Fe, Ni, Cu, Pd, Ag, Mo, W, Pt	101:89910w (1984)		TPD, UPS, XPS, EELS
Nb(110)	113:159426s (1990)	2401000	ESD, TPD, EELS, AES
Mg	110:237526d (1988)	295	XPS, UPS
Ti	112:223896d (1989)	295	XPS, UPS
Mn, O-Mn	110:121980t (1988)	295675	XPS, UPS
<b>Oxidec</b>			
Fe <sub>2</sub> O <sub>3</sub>	118:80333d (1992)		IR, TPD
Fe-Mo-O	113:238760z (1990)		IR
	75:91489d (1971)	251298	Isotherm, kinetics
NiO(100)	117:258892e (1992)	298	HREELS
CeO <sub>2</sub>	117:158185h (1992)	RT	FT-IR
Cr <sub>2</sub> O <sub>3</sub>	116:105450p (1991)	298673	IR
CrO <sub>3</sub> , Cr-Mo-O	114:246758r (1991)	298473	IR
MgO(100)	115:287939q (1991)	90490	HREELS
MgO	107:205681x (1987)	373673	IR
	87:38618s (1977)	3001123	TD
BeO	83:183996k (1975)		IR
CuO	114:50304v (1990)		
CuO/SiO <sub>2</sub>	115:190775v (1991)	295538	IR
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub>	115:121080c (1991)	433623	Isotherm, heat of adsorption
Cu/ZnO/Cr <sub>2</sub> O <sub>3</sub>	102:95188d (1985)	403473	IR
Cu/ZnO/SiO <sub>2</sub> , ZnO/SiO <sub>2</sub>	117:170637q (1992)	295393	FT-IR
Cu-ZnAl <sub>2</sub> O <sub>4</sub> , ZnAl <sub>2</sub> O <sub>4</sub>	112:177859u (1990)	RT523	TPD, FT-IR
	90:210578d (1979)	123	XPS, UPS, AES
ZnO	111:45661t (1989)		IR

(continued)

## Table 4 Continued

Table 4 Methanol Adsorption Literature: Vapor-Phase Adsorption

Solid surface	CA no. (year published)	Temperature (K)	Method
ZnO(10 $\bar{1}$ 0), ZnO(50 $\bar{5}$ 1) ZnO(40 $\bar{4}$ 1), ZnO(0001)	100:67685d (1984) 99:104617s (1983)	300750 300750	TDP, LEED TPD, LEED
TiO <sub>2</sub> (001)	113:159424q (1990)	300800	UPS, TD
TiO <sub>2</sub> (100)	112:223896d (1989)	295	XPS, UPS
Ti <sub>2</sub> (110), TiO <sub>2</sub> (441)	108:119464t (1988)	298	XPS, UPS, LEED
TiO <sub>2</sub> (anatase)	104:24675r (1985)		FT-IR, microcalorimetry
Ti-Si-O	109:177070t (1988)		
V <sub>2</sub> O <sub>5</sub> , V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	110:199697a (1989)	RT 520	FT-IR
SbVO <sub>4</sub> , CrVO <sub>4</sub>	109:135818n (1988)		FT-IR, TPD
SbVO <sub>4</sub> , Sb <sub>2</sub> O <sub>4</sub>	94:128079r (1980)		TPD
SbVO <sub>4</sub> , FeVO <sub>4</sub> , CrVO <sub>4</sub> , Co <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub> , Cu <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>	90:128072a (1978)	323383	
MoO <sub>3</sub>	100:92035z (1984)	373	IR
Y <sub>2</sub> O <sub>3</sub>	72:136729p (1970)	293473	IR, electrical conductance
Zeolite			
H-ZSM-5	118:261522k (1993) 113:198719j (1990) 113:151696j (1990) 104:116585q (1986) 101:198644h (1984) 101:98229h (1984) 98:114273v (1983)	323.16 RT 253323 273425 298	Heat and entropy of adsorption FT-IR, NMR, microbalance 13C-NMR QENS Isotherm, kinetics
Na-ZSM-5, K-ZSM-5	113:198719j (1990)	RT	FT-IR, NMR, microbalance
Silicalite	118:261522k (1993)	323.16	Heat and entropy of adsorption
Eu-mordenite	100:216110s (1984)	298	Isotherm, UV, fluorescence
H-mordenite	98:114273v (1983)	263298	ERS, ESES

Zeolite	116:114099h (1992)		IR, QCMM
Na-A, CaNa-A, Na-X, K-X, Na-Y, K-Y	95:131939x (1981)	RT	ESES
CoNa-A	97:101242p (1981)		Mössbauer
FeCaNa-A	98:25143k (1982)	RT373	Mössbauer
Na-Y, H-Y	83:143240c (1975)	298498	IR, NMR, diffusion coefficient
Na-X, Na-Y, Ca-X, Ca-Y	83:33360j (1975)	303373	IR
Clinoptilolite	101:43945h (1984)	298	Microcalbrimetry, isotherm
Carbon			
Active carbon	117:77261c (1992)	273303	Heat and entropy of adsorption
	107:184277c (1987)	298	NMR, self-diffusion coefficient
Ni, Cu, Zn, Cd/active carbon	117:77261c (1992)	273303	Heat and entropy of adsorption
Coal	116:217778h (1992)	284, 303	Isotherm, heat of adsorption
Charcoal cloth	115:240512e (1991)	293	Isotherm
Graphite	106:49272m (1986)	293303	Isotherm, heat of adsorption

(continued)

## Table 4 Continued

Table 4 Methanol Adsorption Literature: Vapor-Phase Adsorption

Solid surface	CA no. (year published)	Temperature (K)	Method
Other adsorbents			
Silica gel	116:114099h (1992)		IR, QCM
	109:237790q (1988)	RT	FT-NIR
Aerosil	105:214310m (1986)	298308	Isotherm
	96:11932p (1981)	308	Isotherm
	89:221387w (1978)	293	Isotherm, TSD
	83:33360j (1975)	303373	IR
Silica-alumina	104:231115y (1986)	413533	Isotherm, heat of adsorption
Alumina	105:159383k (1986)	298473	FT-IR, microcalorimetry
	103:201359t (1985)	RT 473	FT-IR, microcalorimetry
	86:71473t (76)	3001000	TPD, isotopic tracer
Salts			
CsCl, CsBr, CsI	88:198210b (1978)		IR, heat of adsorption
LiCl, NaCl, NaBr, KCl, KBr, KI all on (100) plane	88:12360x (1977)	283313	Isotherm, heat of adsorption
AgI	67:111683c (1967)	283303	Isotherm
Other			
Si(111)	115:240493z (1991)		TD
	106:162977h (1986)		TD
Glass	70:108751e (1969)	303353	Isotherm, heat of adsorption
Lunar soil	88:25931j (1977)	423, 573	Isotherm

a Abbreviations: AES (Auger electron spectroscopy); EELS (electron energy loss spectroscopy); ESD (electron-stimulated desorption); ESES (electron spin-echo spectrometry); ESR (electron spin resonance spectroscopy); FIM (field ion microscopy); FT-IR (Fourier-transform infrared spectroscopy); FT-NIR (Fourier-transform near-infrared spectroscopy); HREELS (high-resolution electron energy loss spectroscopy); IR (infrared spectroscopy); IRAS (infrared reflection adsorption spectroscopy); LEED (low-energy electron diffraction); NMR (nuclear magnetic resonance); PFDMS (pulsed-field desorption mass spectrometry); QCM (quantum chemical molecular model); QENS (quasi-elastic neutron scattering); TD (thermal desorption); TGA (thermal gravimetric analysis); TPD (temperature-programmed desorption); TSD (thermally stimulated depolarization); UHV (ultrahigh vacuum); UPS (ultraviolet photoelectron spectroscopy); UV (ultraviolet spectroscopy); XPS (x-ray photoelectron spectroscopy); RT (room temperature).

b Most under UHV conditions, adsorption/decomposition.

c Adsorption/decomposition/reaction.

some industrially important reactions. Detailed discussion of these reactions can be found in Chapters 4 and 5. Other compounds synthesized from methanol include formic acid,

methyl nitrate, methyl nitrite, methyl hydrogen sulfate, sodium methoxide, methyl acetals, trimethyl phosphine [6, 49], and methanethiol (methyl mercaptan) [50]. Although higher thiols can be made by direct addition of hydrogen sulfide to the corresponding olefins, methanethiol can only be made by substituting the OH group of methanol with SH. The radiolysis of methanol has also been studied [51].

Table 5 Methanol Adsorption Literature: Liquid-Phase Adsorption (Most at Room Temperature)

Solid surface	CA no. (year published)	Solution	Method <sup>a</sup>
Electrode <sup>b</sup>			
Pt(100)	118:155306h (1993)	0.1 M Na <sub>2</sub> CO <sub>3</sub> (aq)	VG, EMIRS
	110:14975y (1988)	0.05 M HClO <sub>4</sub> (aq)	VG
	108:64530d (1987)	0.5 M HClO <sub>4</sub> (aq)	EMIRS
Pt(110)	117:120399t (1992)	0.1 M Na <sub>2</sub> CO <sub>3</sub> (aq)	VG
	108:64530d (1987)	0.5 M HClO <sub>4</sub> (aq)	EMIRS
Pt(111)	110:14975y (1988)	0.05 M HClO <sub>4</sub> (aq)	VG
	108:64530d (1987)	0.5 M HClO <sub>4</sub> (aq)	EMIRS
Pt	110:221362m (1989)	Acid aqueous	
	98:169175v (1983)	1 M HClO <sub>4</sub> (aq)	IRAS
Ni	89:154599b (1978)	KOH (aq)	Radiotracer
Bi	83:67801u (1975)		
Ir	72:128018r (1970)	KOH, phosphate (aq)	Isotherm
Other			
Montmorillonite	97:99006u (1982)	Benzene-heptane	
Active carbon	110:219678a (1989)	Toluene	Microcalorimetry
Charcoal cloth	115:240512e (1991)	Water	Isotherm
Coal	110:219678a (1989)	Toluene	Microcalorimetry

<sup>a</sup> Abbreviations: EMIRS (electromodulated infrared reflectance spectroscopy); IRAS (infrared reflection adsorption spectroscopy); VG (voltammogram).

<sup>b</sup> Adsorption/reaction.

## 2.3.2

### Chemical Hazards

Methanol is incompatible with oxidants in general. Various hazardous reactions involving methanol have been reported [5254]. They are listed in Table 7.

## 2.3.3

### Compatibility with Industrial Materials

Methanol is considered noncorrosive to most structural metals and alloys. Carbon steel is a satisfactory material commonly used for making methanol containers and handling equipments. Aluminum and its alloys have also been used [35,55]. However, anhydrous methanol at its boiling point has been reported to be corrosive to aluminum and its alloys [55,56]. Copper was reported to be resistant to methanol liquid from room temperature to its boiling point and to methanol vapor at 108°C [56]. Copper lining has been used in autoclaves for

Table 6 Some Industrially Important Reactions Using Methanol as Feedstock

Type of reaction	Product	Reaction equation
Oxidative dehydrogenation	Formaldehyde	$\text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$
Addition to unsaturated bond	Methyl tert-butyl ether (MTBE)	$\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{C} = \text{CH}_2 \rightarrow (\text{CH}_3)_3\text{COCH}_3$
Carbonylation	Acetic acid	$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$
	Acetic anhydride	$\text{CH}_3\text{OH} + \text{CH}_3\text{COOH} + \text{CO} \rightarrow (\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O}$
Esterification	Methyl methacrylate	$\text{CH}_3\text{OH} + \text{CH}_2 = \text{C}(\text{CH}_3)\text{COOH} \rightarrow \text{CH}_2 = \text{C}(\text{CH}_3)\text{COOCH}_3 + \text{H}_2\text{O}$
	Dimethyl terephthalate	$2\text{CH}_3\text{OH} + \text{HOOC}(\text{C}_6\text{H}_4)\text{COOH} \rightarrow \text{CH}_3\text{OOC}(\text{C}_6\text{H}_4)\text{COOCH}_3 + 2\text{H}_2\text{O}$
Etherification	Dimethyl ether	$2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$
Dehydration	Ethylene	$2\text{CH}_3\text{OH} \rightarrow \text{CH}_2 = \text{CH}_2 + 2\text{H}_2\text{O}$
	Gasoline	$n\text{CH}_3\text{OH} \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
Substitution	Methyl Halides	$\text{CH}_3\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{I} + \text{H}_2\text{O}$
	Methyl amines	$\text{CH}_3\text{OH} + \text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$
		$\text{CH}_3\text{OH} + \text{CH}_3\text{NH}_2 \rightarrow (\text{CH}_3)_2\text{NH} + \text{H}_2\text{O}$
		$\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{NH} \rightarrow (\text{CH}_3)_3\text{N} + \text{H}_2\text{O}$
	Methanethiol	$\text{CH}_3\text{OH} + \text{H}_2\text{S} \rightarrow \text{CH}_3\text{SH} + \text{H}_2\text{O}$

methanol carbonylation to acetic acid operated at 300°C and 25.3 MPa (250 atm) in the presence of nickel carbonyl and iodine as catalysts [44].

Collections of corrosion data can be found in References 55-57. Reference 55 also gives sources of literature data. Metals reported as incompatible with methanol include aluminum against anhydrous methanol at its boiling point [55,56], lead against 96-100% methanol at room temperature [56], and magnesium against pure methanol at room temperature [55]. Titanium and its alloys suffer from stress corrosion cracking in methanol [55], and zirconium alloys suffer from stress corrosion cracking in mixtures of methanol and hydrochloric acid and in mixtures of methanol and iodine [55].

Nonmetal structural materials, including glass, porcelain, ceramic bricks and tiles, cements, concrete, and graphite, have been reported to be methanol compatible [56]. Compatibility of polymeric materials with methanol has also been reported [58,59]. Table 8 serves as a general classification. A more complete list can be found in Reference 59. The temperature effect can be found in Reference 58 for some plastics in general.

Table 7 Hazardous Reactions Involving Methanol

	Reaction counterpart
Explosive reaction	Air (mixture may explode at 0.181 MPa and 120°C) Chloroform (when heated) Diethyl zinc
Violent reaction	Acetyl bromide (with HBr evolution) Alkyl aluminum salts or solutions Beryllium hydride Chloroform with sodium hydroxide or potassium hydroxide Chromium trioxide Cyanuric chloride Hydrogen with Raney Ni catalyst (hydrogenolysis of methanol) Iodine with mercuric oxide and ethanol Lead perchlorate Nitric acid Phosphorus(III) oxide Perchloric acid Potassium tert-butoxide (ignition)
Chemically incompatible	Barium perchlorate Bromine Carbon tetrachloride with Al, Mg, or Zn (2 h induction period for Zn) Chlorine Dichloromethane Hydrogen peroxide Metals, including Al, Mg, K, Zn (mixtures with Al, K, or Mg powder are capable of powerful detonation) Methylene chloride (flammable) Oxidants Sodium hydrochlorite Water at 3040% methanol (can be ignited by a static discharge)

Source: From References 5254.

## 2.4

### Specification and Analysis

Methanol (synthetic, 99.85%) is readily available commercially. The four most accepted sets of specification are given in Table 9 [6062]. Common impurities are water, acetone, formaldehyde, ethanol, methyl formate, and traces of dimethyl ether, methylal, methyl acetate, acetaldehyde, carbon dioxide, and



Table 8 Compatibility of Polymeric Materials with Methanol

	Thermoplastics	Thermosets	Elastomers
Compatible	Polyethylene (LDPE, HDPE)	Epoxides	Chloroprene
	Polypropylene (PP)	Phenolics (PF)	(neoprene)
	Chlorinated polyether	Polyimides	Silicones
	Polyacetals	Polybutadiene	Fluorosilicone
	Fluoroplastics (PTFE, ETFE, FEP, PVDF, ECTFE, PTFCE, PFA)	Melamine formaldehyde resin (MF)	Ethylene-propylene
	Polymethylpentene (PMP)		
	Polycarbonates (PC)		
Less compatible	Polyvinylchlorides (PVC)	Polyurethanes (PU)	
	Polyurethanes (PU)	Polyesters, unsaturated	Nitrile rubber (NBR)
	Styrene-based polymers	Furan	
	Polyoxymethylene (acetal, ACL)	Diallyl phthalate (DAP)	
	Polyesters (PET)		
	Polysulfones (PSF)		
Incompatible	Polyamides (nylon)		
	Polymethyl methacrylate (PMMA, acrylics)		Styrene based
	Cellulose		

Source: From References 58 and 59.

Table 9 Methanol Specifications

Property	Grade A [60]	Grade AA [60]	ACS [61]	ASTM [62]
Methanol content	$\geq 99.85$ wt%	$\geq 99.85$ wt%	$\geq 99.8$ wt%	$\geq 99.85$ wt%
Water	$\leq 0.15$ wt%	$\leq 0.10$ wt%	$\leq 0.10$ wt%	$\leq 0.10$ wt%
Acetone		$\leq 20$ ppm	$\leq 10$ ppm	$\leq 30$ ppm
Ethanol		$\leq 10$ ppm		
Formaldehyde			$\leq 10$ ppm	
Acetaldehyde			$\leq 10$ ppm	
Hydrocarbon				To pass test
Acetone and aldehydes	$\leq 30$ ppm	$\leq 30$ ppm		
Titrateable acid	$\leq 30$ ppm	$\leq 30$ ppm	$\leq 0.3$ $\mu$ Eq/g	$\leq 30$ ppm
Titrateable base			$\leq 0.2$ $\mu$ Eq/g	
Specific gravity				
20/20°C	0.7928	0.7928		0.79200.7930
25/25°C				0.78830.7893
Odor	Characteristic	Characteristic		Nonresidual
Color, Pt-Co (APHA)	$\leq 5$	$\leq 5$	$\leq 10$	$\leq 5$
Appearance	Clear	Clear	Clear	
Residue after evaporation	$\leq 10$ mg/L	$\leq 10$ mg/L	$\leq 0.001\%$	$\leq 50$ mg/L
Permanganate time	$\geq 30$ min	$\geq 30$ min	To pass test	$\geq 50$ min
Carbonizable impurities by sulfuric acid, color, Pt-Co (APHA)	$\leq 30$	$\leq 30$	To pass test	$\leq 50$
Distillation range (1 atm)	$\leq 1^\circ\text{Ca}$	$\leq 1^\circ\text{Ca}$		$\leq 1^\circ\text{Ca}$
Solubility in water			To pass test	

a Must include  $64.6 \pm 0.1^\circ\text{C}$ .

ammonia [63]. The U.S. federal grade AA has specific limits on acetone and ethanol contents; the American Chemical Society (ACS) reagent grade has limits on acetone, formaldehyde, acetaldehyde, and base contents.

The comparative ultraviolet absorbance test provides a quick and satisfactory quality check for methanol for general uses [6]. The method relies on the featureless response of methanol to UV and is sensitive to traces of aromatic and most other organic compounds. The ACS absorbance test [61] checks the measured sample absorbance as  $\leq 0.001$  from 280 to 400 nm,  $\leq 0.04$  at 260 nm,  $\leq 0.10$  at 240 nm,  $\leq 0.20$  at 230 nm,  $\leq 0.40$  at 220 nm, and  $\leq 0.80$  at 210 nm. The absorbance curve throughout the range 210-400 nm should be smooth and without extraneous impurity peaks. A standard 1.00 cm cell is used, and pure water is used as the reference. Other ACS test methods can be found in Reference 61. Methods for methanol purification, especially the removal of water and

acetone, are summarized by Perrin and Armarego [63]. Some methanol-related American Society for Testing and Materials (ASTM) methods are as follows:

D1152-84 (06.03)	Specification
E346-87 (15.05)	Analysis of methanol
D1612-86 (06.03)	Acetone in methanol
D1613-85 (06.03)	Acidity in volatile solvents
D1364-86 (06.03)	Water in volatile solvents
D1353-86 (06.03)	Nonvolatile matter in volatile solvents
D769-85 (15.07)	Odor of methanol
D1363-84 (06.03)	Permanganate time
D1209-84 (06.03)	Color, Pt-Co scale (APHA, American Public Health Association)
D1078-86 (06.03)	Distillation range

There are various market products of methanol for specific laboratory uses. That for a solvent for spectrophotometry should pass the ACS absorbance test [61]. That for high-performance liquid chromatography should pass the absorbance test and yield no peaks greater than 0.005 absorbance unit in the ACS gradient elution test [61]. That for pesticide residue analysis should pass gasliquid chromatography interference test with chlorinated hydrocarbons (as heptachlorepoxy)  $\leq 10$  ng/L, sulfur (as parathion)  $\leq 500$  ng/L, and phosphorus (as parathion)  $\leq 100$  ng/L. There are also products extremely low in metal impurities ( $\leq 1$  ppm total heavy metals) for semiconductor processing, or extremely low in water content ( $\leq 0.005\%$ ). Deuterium- and carbon 13-exchanged methanol,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ ,  $\text{CD}_3\text{OD}$ ,  $^{13}\text{CH}_3\text{OH}$ , and  $^{13}\text{CD}_3\text{OD}$ , are also available. The degree of exchange usually exceeds 99%.

## 2.5

### Handling Aspects:

#### Fire Hazards, Storage and Transportation, and Spillage

### 2.5.1

#### Fire Hazards

Methanol is highly inflammable, having a National Fire Protection Association (NFPA) fire hazard rating of 3 [54] in a scale from 0 to 4 (0 corresponds to noncombustible and 4 to extremely inflammable). Methanol vapor evolved at room temperature may form an explosive mixture with air over a wide range of concentration (5.544%). Methanol has a flash point of 11°C and an autoignition temperature of 464°C. It has a reported burning rate of 1.7 mm/min [17].

Because of the explosive nature of methanol, electrical devices and equipment used in the area of methanol must be in accordance with relevant regulations.

Open flame and devices capable of igniting the vapor must not be used. Also, pure methanol has a very low electrical conductivity. Electrostatic charging should be prevented when handling pure methanol. The electrical hazard of methanol is rated class 1, group D [17].

Methanol fire is difficult to fight because the flame is usually invisible in day-light. Flashback of fire along the vapor trail may also occur. Effective extinguishing agents for methanol fire are dry chemical powder, alcohol foam, and carbon dioxide [17]. Water may be ineffective on fire but is useful in cooling exposed containers to reduce explosion potential. Formaldehyde and carbon monoxide may be formed from methanol burning when the oxygen supply is insufficient. Respirators must therefore be used when fighting methanol fires in enclosed areas.

## 2.5.2

### Storage and Transportation

Because of its inflammability and toxicity, methanol must be handled with precaution. Methanol loading and unloading can be handled by pumping. If pressure loading and unloading are to be practiced, an inert gas must be used. Compressed air should never be used for methanol handling.

Methanol in small amounts is usually stored in glass bottles or sheet-metal cans. Plastic bottles made of high-density polyethylene or polypropylene are also used. A metal bucket should be used when carrying methanol in a glass or plastic bottle. Steel drums of up to 200 L each are used for storage and transportation of methanol.

Large-scale methanol storage usually uses cylindrical tanks similar to those used for petroleum products. A floating-roof design is usually the choice. If a fixed-roof tank is used, an inert gas pad must be used to prevent the possible formation of an explosive mixture above the liquid. Tanks in a tank farm are usually enclosed by dikes and protected by water cannons and fire-extinguishing systems.

Inland transportation of methanol usually uses tank trucks, rail tank cars, or waterway vessels. The shipping containers should be dry and clean before loading. If the containers are not specialized for methanol transportation, analysis is usually required for each delivery. Each container must be appropriately labeled (such as U.S. Department of Transportation red label) for inflammable liquids. Additional cautionary labels (such as poisonous chemical) may be required by local authorities. Overseas transportation is by tankers. Regulations governing methanol transportation in selected countries can be found in Reference 6.

### 2.5.3

#### Spillage

With methanol spillage, fire hazard is the first concern. Open flame and ignition sources in the nearby area should be shut off immediately. All persons should withdraw to a safe distance.

A small amount of spill can be mopped up and run to the waste with excess running water. Gloves and respirators, if necessary, should be worn in the clean-up. The area should be well ventilated to dispel methanol vapor.

At a large-scale spill, most likely as a result of a transportation accident, local authorities and fire department should be notified immediately. People in the area should be evacuated. Action, whenever possible, should be taken to stop the methanol discharge and to isolate the damaged container from the rest. Rescuers should stay upwind and use water spray to knock down the vapor and disperse the liquid. Local health and pollution control agencies should be notified, and the potential of methanol drainage to surface or underground water that may lead to the contamination of drinking water should be evaluated and monitored if needed.

## 2.6

### Toxicity, Occupational Health, and Environmental Concerns

#### 2.6.1

##### Toxicity

Methanol is toxic under acute and chronic exposure. Poisoning may occur from ingestion, inhalation, or skin absorption. Methanol is an irritant to mucous membrane, skin, and eyes. Liquid contact and vapor exposure and inhalation should be avoided. The most commonly known poisoning effect of methanol is visual impairment or blindness, often as a result of ingestion. Methanol is also a teratogen and a narcotic [54].

Sensitivity to methanol poisoning varies widely from person to person. There were cases in which no permanent damage resulted from drinking large quantities (200500 ml) of methanol [64,65]. In another case, however, permanent blindness was reported as a result of methanol consumption of only 4 ml [66]. Although the fatal dosage is usually set at 100250 ml [67], death from ingestion of as little as 30 ml has been reported [68]. Continuous exposure to 50,000 ppm methanol vapor for 12 h will probably also cause death [17]. Cases of vision impairment and death resulting from methanol absorption or inhalation were cited in early reports [69]. Collections of methanol toxicity reports can be found in References 68 and 70.

Whether methanol intake is via ingestion, inhalation, or skin absorption, the same symptoms may develop. The acute effects are weakness, headache, fatigue, dizziness, nausea, and abdominal pain, followed by characteristic visual impairment, including blurred or double vision, mydriasis, and photophobia. In severe cases, usually from ingestion, convulsions, circulatory collapse, respiratory failure, and death may also follow. Within days, the visual impairment may either ease or develop into permanent blindness. Damage to the central nervous system may be another chronic effect.

The diagnosis of methanol intoxication includes the observation of the preceding symptoms. The combination of the characteristic visual disturbances and a history of methanol exposure is usually considered a confirmative diagnosis. Confirmation can also be reached by a urine test with positive formic acid or methanol presence.

The human toxicology of methanol has been studied [6,71,72]. The skin absorption rate has been reported to be 0.19 mg/cm<sup>2</sup>/min [73]. Methanol vapor uptake by the lungs is effective, usually 70-80% (74). In the liver, methanol goes through oxidation metabolism catalyzed by alcohol dehydrogenase (an enzyme), producing toxic formaldehyde and formic acid. The accumulation of formic acid leads to acidosis, damaging the nervous system, particularly the optic nerves, and the retina. In the copresence of ethanol, ethanol is selectively metabolized by alcohol dehydrogenase over methanol; this delays methanol intoxication and allows detoxication by the natural elimination of methanol via respiration and urination. The methanol elimination half-life is about 23 h [6]. Because of the slow elimination, methanol can be regarded as a cumulative poison [68]. Chronic exposure may result in sufficient methanol accumulation in the body, and illness.

First aid for liquid methanol contact with eyes or skin is immediate water flush for 15 min. For vapor exposure and inhalation, the victim should be removed to fresh air and given artificial respiration if needed. If ingestion is suspected, a physician should be called and treatment should be initiated as quickly as possible. Effective measures for conscious patients include inducing vomiting [6,17], orally taking 30-40 ml ethanol to delay methanol metabolism [6,49], and orally taking 510 g of sodium bicarbonate (baking soda) in a glass of water every hour to combat acidosis [75].

### 2.6.2 Occupational Health

Methanol is classified by the NFPA to be of slight health hazard [54], with a rating of 1 in a scale from 0 to 4 (0 corresponds to no significant health hazard and 4 to extreme health hazard). Although methanol vapor is not particularly health hazardous, its presence deserves special concerns for having no natural

alarms: methanol vapor is colorless and has only a mild alcoholic odor. There is no clear or reliable odor threshold for methanol vapor. The reported values vary from 100 [17] to 2000 ppm [76]. A collection of reports on methanol odor threshold is given in Reference 76. Furthermore, the alcoholic odor of methanol may not be differentiable from that of other less harmful alcohols. Test methods for methanol vapor concentration in air have been released from NIOSH (Set E) [77] and ASTM (D4597 and D4598) [78]. Methanol vapor concentrations from 50 to 6000 ppm at workplaces have been reported [76]. Some recommended levels for maximum methanol vapor exposure are given in Table 10. The maximum level of 200 ppm is also observed in Germany [77], Canada [52], and Sweden [77]. Chronic exposure to methanol vapor of 12008300 ppm may cause vision impairment [79]. Exposure to 3653080 ppm may cause blurred vision, headache, dizziness, and nausea [69].

If methanol handling is a routine practice, the workplace should be ventilated adequately. Whenever possible, methanol handling should be practiced in a confined area with forced venting so that vapor does not spread into the workroom. Workers handling methanol should wear goggles or face shields for eye protection and gloves and protective clothing to prevent skin contact. If workers must enter an enclosed area or vessel with high methanol vapor concentrations, respirators with supplied air should be used.

Workers regularly handling methanol should receive a physical examination every 6 months, including visual test, neurological evaluation, and tests of liver and kidney functions. The alarm concentration of methanol in urine has been reported to be 10 µg/ml [72]. Individuals with disease of the eyes, liver, kidneys, and lungs should avoid methanol handling and exposure.

### 2.6.3

#### Environmental Concerns

Methanol is readily biodegradable and is not particularly environmentally harmful. The most serious concern about methanol pollution is the contamination of

Table 10 Recommended Levels of Maximum Methanol Vapor Exposure<sup>a</sup>

OSHA	PEL 200 ppm TWA	IDLH 10,000 ppm
ACGIH	TLV 200 ppm TWA	STEL 250 ppm (skin), 60 min
NIOSH	REL 200 ppm TWA	Ceiling 800 ppm, 15 min

<sup>a</sup> Abbreviations: OSHA, Occupational Safety and Health Administration; ACGIH, American Conference of Governmental Industrial Hygienists; NIOSH, National Institute for Occupational Safety and Health; PEL, permissible exposure level; TLV, threshold limit value; TWA, time-weighted average, up to 10 h workday, 40 h workweek; IDLH, immediately dangerous to life or health; STEL, short-term exposure limit.

Source: From Reference 54.



drinking water or its sources. The suggested method for methanol liquid and vapor disposal is incineration [52,77]. Methanol in wastewater can be effectively eliminated by biodegradation [6]. The biological oxygen demand (BOD) has been reported to be 0.61.12 kg/kg in 5 days [17]. A list of biological effects of methanol on bacteria, algae, protozoa, arthropoda, fish, mammalia, and human, as well as a collection of water pollution-related reports, can be found in Reference 76. The methanol content of wastewater should not exceed 3.6 mg/L as suggested by the U.S. Environmental Protection Agent (EPA) [17,77]. Methanol is in the Community Right to Know List, and the EPA Toxic Substances Control Act Inventory and Genetic Toxicology Program [68].

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### 3

## Production of Methanol

J. R. LeBlanc, Robert V. Schneider, III, and Richard B. Strait  
The M. W. Kellogg Company, Houston, Texas

### 3.1

#### History

It is reported [1] that methanol was first isolated in 1661 by Sir Robert Boyle by rectifying crude vinegar over milk of lime. Independently, both Justus Von Liebig (1803-1873) and J. B. A. Dumas (1800-1884) determined the composition of methanol. As a result of their work, the term "methyl" was introduced into chemistry in 1835.

Commercially, the first process for the production of methanol was by the destructive distillation of wood, thus the source of the common name wood alcohol. Wood was the source of methanol from about 1830 until the mid-1920s [2]. It was at that time that a process for the synthetic manufacture of methanol was put into commercial operation by Badische Anilin-und-Soda-Fabrik (BASF) in Germany. Before the BASF process, methanol was considered a specialty chemical. With the introduction of synthetic methanol, the supply of methanol greatly increased. In the early 1920s in the United States, the demand for methanol was some 15,000-30,000 t per year. By the early 1940s, the demand in the United States increased to over 180,000 t. This sharp increase reflected the use of methanol as a chemical intermediate, a feedstock for downstream processes.

BASF introduced the first large-scale commercial methanol plant in 1923. Perhaps this was not too surprising because BASF first commercialized the

process for making synthetic ammonia 10 years earlier, in 1913. The process for making methanol used a zinc chromite catalyst over which a mixture of hydrogen and carbon oxides was reacted at temperatures of 300–400°C and pressures of 25–35 MPa (250–350 atm). The synthesis feed gas was coal derived through the water-gas shift reaction.

In the United States, a subsidiary of the DuPont Company, Lazote, Inc., made synthetic methanol at Belle, West Virginia. The Belle operation was part of the ammonia plant at the site. The methanol production was actually a step in the ammonia process for removing carbon monoxide, which was an impurity in the ammonia synthesis gas. Commercial Solvents was the first to employ the high-pressure synthesis process, developed by BASF, in the United States. The plant, located in Peoria, Illinois, began operation a few months after the Lazote plant at Belle. The Commercial Solvents plant used an off-gas from a fermentation operation. The off-gas contained carbon dioxide and hydrogen from the production of butanol from corn. This first of a kind plant in the United States was rated at about 4000 t per year.

Most of the methanol made until the end of World War II was produced from coke-derived synthesis gas as well as off-gases from fermentation, coke ovens, and steel furnaces. One of the most significant changes in commercial methanol manufacture was the use of natural gas as the feedstock source. There were a number of factors that contributed to the use of natural gas. A natural gas facility produced a higher quality synthesis gas with fewer impurities, and in the United States natural gas was available in almost unlimited quantities. In 1946, about 71% of the carbon monoxide used in feeding methanol plants was derived from coke or coal. By 1948, about 77% was obtained from natural gas [2].

By the late 1960s, medium- and low-pressure methanol technology was in commercial use [3]. This new technology was based on the use of copper zinc catalysts.

Contributing to the success of the new methanol catalysts was the ability to clean the natural gas feed to very low impurity levels. Sulfur, which typically is the major impurity, can be removed to levels of less than 0.5 ppm in the natural gas feed. This means even lower levels in the synthesis gas. Such impurities, which are poisons to the highly active catalyst, must be removed to these low levels for the operation to be efficient.

ICI, Ltd. of the United Kingdom began manufacturing methanol with the new technology in 1966. The plant, with 400 t per day capacity, operated at 5 MPa (50 atm) and used centrifugal compression equipment. Here again the history of ammonia and methanol production crossed paths. In the mid-1960s, the M. W. Kellogg Company first commercialized the large-scale single-train ammonia plant using centrifugal compression equipment. The use of centrifugal com-

pression equipment in producing methanol was made possible through low-pressure operation over the copper zinc catalyst. The operation benefitted from applying the compression know-how gained in ammonia synthesis. Through the use of the low-pressure copper synthesis catalysis and by using the large-capacity single-train concept, the manufacture of methanol became much more cost effective than earlier plants using the high-pressure technology. Economy of scale, reduced energy consumption, and improved plant reliability made the new low-pressure plants much more economical. Thus, with few exceptions, since about 1970 new methanol plants have been based on the low- and medium-pressure synthesis technologies.

Today, methanol technology is available from several sources, all of which use low to medium synthesis pressure technology. ICI provides methanol technology through several licensee engineering companies. ICI provides the synthesis catalyst for their technology. Lürgi of Germany provides methanol technology through its own engineering services. The Lürgi technology is based on using the Süd-Chemie, AG methanol synthesis catalyst. The M. W. Kellogg Company of the United States provides methanol technology worldwide.

The Kellogg technology is based on using BASF low-pressure methanol synthesis catalyst. Mitsubishi Gas Chemical of Japan provides methanol technology based on the use of its own methanol catalyst. Topsøe of Denmark, using its own catalyst, is a supplier of methanol technology as well. All these currently available methanol technologies use a copper-based synthesis catalyst.

## 3.2

### Thermodynamics and Kinetics of Methanol Synthesis

#### 3.2.1

##### Thermodynamics

Methanol is typically synthesized in the gas phase over a heterogeneous catalyst from a gas containing a combination of hydrogen, carbon monoxide, and carbon dioxide. Synthesis can be from either of the following chemical reactions



or



On an industrial scale, methanol is synthesized from both reactions (1) and (2) simultaneously. Reaction (1) is exothermic, with a heat of reaction equal to 21.66 kcal/g-mol at 298K. Reaction (2) is likewise exothermic, with a heat of reaction equal to 11.83 kcal/g-mol. Both reactions exhibit a decrease in volume (reduction in moles as the reaction proceeds to the right), and since both

are exothermic, methanol synthesis is favored by increasing pressure and decreasing temperature.

A reverse water-gas shift is also promoted over catalysts that promote methanol synthesis and thus must also be considered. This reaction proceeds according to



Reaction (3) as it proceeds toward CO production is endothermic, with a heat of reaction equal to 9.84 kcal/g-mol. In all the preceding cases, heats of reaction may be easily calculated at any temperature from heats of formation tables, where

$$\Delta H_{\text{RXN}} = \sum(H_F^0 \text{ products}) - \sum(H_F^0 \text{ reactants})$$

Reaction (2) is simply the sum of reactions (1) and (3), so even though all reactions progress simultaneously, only reactions (1) and (3) are considered independently, with maximum conversion of syngas to methanol limited by thermodynamic equilibrium.

Equilibrium compositions may be calculated by simultaneous solution of the equations that describe the equilibrium constants for the given reactions (1) and (3):

$$K_{\text{reverse shift(3)}} = \frac{[p^*\text{CO}][p^*\text{H}_2\text{O}]}{[p^*\text{CO}_2][p^*\text{H}_2]}$$

and likewise.

$$K_{\text{methanol synthesis(1)}} = \frac{[p^*\text{CH}_3\text{OH}]}{[p^*\text{CO}][p^*\text{H}_2]^2}$$

When accounting for the nonideality of gases at elevated pressures, the concept of fugacity should be taken into account, where

$$f_i = p_i^* \phi_i$$

In this equation,

$f_i$  = fugacity of the  $i$ th component  
 $p_i^*$  = partial pressure of the  $i$ th component  
 $\phi_i$  = fugacity coefficient of the  $i$ th component

Taking the concept of fugacity into account, these equilibrium expressions can thus be written as

$$K_3 = \frac{[f\text{CO}][f\text{H}_2\text{O}]}{[f\text{CO}_2][f\text{H}_2]} = K \phi_3 K_{p_3}$$

$$K_3 = \frac{[p^*CO][p^*H_2O]}{[p^*CO_2][p^*H_2]} \frac{[\phi CO][\phi H_2O]}{[\phi CO_2][\phi H_2]}$$

and

$$K_1 = \frac{[fCH_3OH]}{[fCO][fH_2]^2} = K\phi_1 K_{p_1}$$

$$K_1 = \frac{[p^*CH_3OH]}{[p^*CO][p^*H_2]^2} \frac{[\phi CH_3OH]}{[\phi CO][\phi H_2]^2}$$

Fugacity coefficients can be estimated by assuming ideal solutions and using critical temperatures and pressure for the various components to arrive at approximate values for  $\phi_i$  from generalized charts (see Ref. 4) or can be calculated from some appropriate equation of state.

Several convenient temperature-dependent equations for calculating K values are readily available from the literature. For the reader's convenience, suitable examples that show reasonable agreement with handbook values are given.

For  $K_1$ , Thomas and Portalski derived the expression [5]

$$\log K = \frac{3921}{T} - 7.971 \log T + 0.002499T - 2.953 \times 10^{-7} T^2 + 10.2$$

where T is in degrees Kelvin. For  $K_3$ , Bissett suggests the relationship [6, 7]

$$K_3 = e[13.148 - 5639.5/T - 1.077 \ln T - 5.44 \times 10^{-4}T - 1.125 \times 10^{-7}T^2 + 49,170/T^2]$$

where T is in degrees Kelvin.

### 3.2.2

#### Catalysts

Originally, industrial synthesis of methanol was over a zinc oxide-chromium oxide catalyst that was operated at a nominal pressure of about 35 MPa (350 atm) and temperatures up to about 450°C. This catalyst unfortunately had a tendency to promote the exothermic methanation reaction ( $CO + 3H_2 \rightarrow CH_4 + H_2O$ ) under certain conditions, which led in some instances to severely overheated reactors. This characteristic plus the high cost of compression and relative nonselectivity of the high-pressure process made it uneconomical following the introduction of low-pressure synthesis in the 1960s.

Low-pressure methanol synthesis, first introduced commercially by ICI of England, is based on a copper oxide-zinc oxide-alumina catalyst that operates over a much lower pressure range (510 MPa nominally) and at considerably lower temperatures (200-280°C). The copper-based family of methanol synthesis catalysts is extremely active, as well as selective, and is used in vapor-phase

methanol synthesis as well as the more recently introduced liquid-phase processes. The copper-zinc-alumina family of methanol synthesis catalysts available today typically exhibits formulations within the following ranges:

Copper oxide, 60-70%

Zinc oxide, 20-30%

Alumina, 5-15%

Low-pressure methanol synthesis catalyst is a well-proven product that is commercially available from a number of reputable suppliers, including BASF, ICI, United Catalysts/Süd-Chemie, and Haldor-Topsøe. In the past, methanol synthesis catalyst was available from these suppliers as part of a process licensed to the end user, although today this practice is no longer universally applied.

These catalysts are manufactured in tablet form (with cylinder sizes generally ranging between  $5.5 \times 3.5$  and  $5 \times 5$  mm) and delivered to the end user in their oxide form. They must then be reduced in situ by passing a controlled concentration of  $H_2$  (around 1 mol%) in a circulating carrier gas, such as nitrogen or methane, over the catalyst bed or beds in question. Maximum temperatures during reduction should be limited typically to 230°C or less.

Reduction or activation must be carefully controlled to preserve copper crystallite size and ensure an optimal catalyst initial activity and life. Proper catalyst activation has time and again been proven to benefit the user by yielding lower by-product makes, higher activities (close approaches to thermodynamic equilibrium), and longer lives.

Although the copper-based catalysts operate under much milder conditions than the high-pressure zinc-chrome catalysts, they are much more susceptible to poisoning and deactivation. The copper-based catalysts are particularly sensitive to sulfur and chlorine, which permanently deactivate the catalyst. Typically, gas feed-based plants (including natural gas and liquid propane gas, LPG, feeds) contain cobalt oxide-molybdenum oxide/zinc oxide guard systems that efficiently remove sulfur as  $H_2S$  to levels below 0.1 ppmv, which in turn results in a synthesis section feed containing less than 0.025 ppmv sulfur. Sulfur is absorbed by both copper and zinc on the surface of the catalyst, and to a certain extent, the catalyst has some ability to protect itself. The levels of clean-up quoted above are not difficult to achieve and generally result in acceptable synthesis catalyst lives that typically range between 2 and 4 years, although many charges have lasted less and a few have lasted more. Chlorine is a more virulent catalyst poison; absorption results in a loss of copper surface area by a mechanism similar to sintering whereby a large number of small copper crystallites are transformed into a smaller number of much larger crystallites; this results in a loss in active copper surface area and an attendant loss in catalyst activity. For achieving a normally expected catalyst life, the chlorine content of the syn-



thesis section feed should be less than half of the sulfur content after cleanup in the purified feed. Unusually high levels of chlorine in the front-end feed gas can be removed by specially formulated chlorine guard absorbents. Particularly with partial oxidation feeds containing high concentrations of CO, iron carbonyl may enter the synloop whereby it is subsequently dissociated over the copper catalyst, leaving substantial deposits of iron that can be expected to lead to excessive by-product formation via the Fischer-Tropsch reaction.

Typically, the copper-based family of methanol synthesis catalysts are extremely selective. Methanol yields are high relative to organic by-products, with generally over 99.5% of the converted CO + CO<sub>2</sub> present as methanol in the crude product stream. H<sub>2</sub>O, of course, is normally a by-product, with a resultant concentration in the crude product that is influenced by the ratio of CO<sub>2</sub> to CO in the methanol synthesis reactor feed stream. Hydrocarbon by-products typically are present in concentrations of less than 5000 ppm(w) and consist of such compounds as the following:

Higher alcohols including ethanol, i/n-propanol, and i/n-butanol

Dimethyl ether

Methyl formate

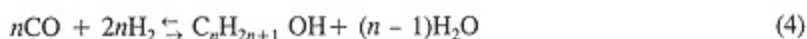
Acetone and other ketones

Aldehydes

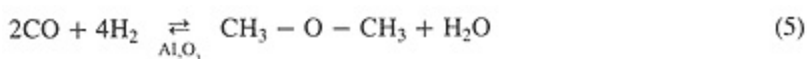
Various paraffinic hydrocarbons, including through C<sub>20</sub><sup>+</sup> waxes

The aforementioned by-products are formed by the following chemical reactions [7]:

Higher alcohols:



Dimethyl ether:



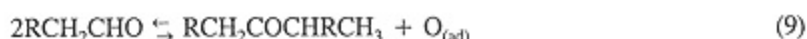
Methyl formate/esters:



and



Ketones:

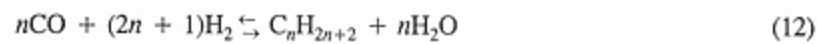




Paraffinic hydrocarbons and waxes (via Fischer-Tropsch):



and generally



High catalyst space times and operating temperatures tend to influence the degree of by-products observed in the crude methanol produced in the commercial synthesis unit. Therefore, as the catalyst ages and operating temperatures are adjusted upward to maintain production, the by-product concentration tends to increase, placing additional load on the purification train, which has the requirement of producing a specification-grade methanol product. Space times (residence times) are generally more a function of the particular synthesis section design being utilized by a given operator.

### 3.2.3

#### Kinetics

Commercial methanol synthesis processes are generally offered under license by various process designers and/or catalyst suppliers. Each has developed its own approach to modeling the synthesis converter or converters, which is usually based upon some type of proprietary kinetic model. Many kinetic models have been postulated in the literature for methanol synthesis. These models are generally of the Langmuir-Hinshelwood type, based on a consideration of the rate-limiting step in the catalytic processes of absorption, reaction, and desorption. One model postulated by Natta et al. [8] and given in terms of fugacities is

$$r = f_{\text{CO}}f_{\text{H}_2}(f_{\text{CH}_3\text{OH}}/K_{\text{eq}})(A + Bf_{\text{CO}} + Cf_{\text{H}_2} + Df_{\text{CH}_3\text{OH}})$$

This kinetic model considered both ZnO-Cr<sub>2</sub>O<sub>3</sub> and ZnO-CuO/Cr<sub>2</sub>O<sub>3</sub> catalysts operating in a temperature range of about 330-390°C. Pressure in this case was upward of 30 MPa (300 atm).

A more recently derived expression suitable for use with low-pressure methanol synthesis catalyst is given by Seyfert [9]:

$$r = f_{\text{CH}}f_{\text{H}_2}^2 - f_{\text{CH}_3\text{OH}}/K_{\text{eq}}(A + Bf_{\text{CO}} + Cf_{\text{H}_2} + OEf_{\text{CO}}f_{\text{H}_2} + Ff_{\text{CO}_2})^2$$

There is much discussion regarding the influence of CO<sub>2</sub> in the methanol synthesis reaction, but today it is generally accepted that CO<sub>2</sub> plays an important role in the kinetics of methanol synthesis. Note that the earlier model by

Natta had no CO<sub>2</sub> term, whereas the Seyfert model accounts for the influence of CO<sub>2</sub> on the rate of methanol synthesis. In the Seyfert model, the rate is expressed in terms of fugacities (as with the Natta expression) and  $r = \text{kg-mol MeOH/kg-cat-h}$ . A, B, C, D, E, and F are rate parameters that have been determined by Seyfert for the BASF low-pressure Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst. Variation in these parameters as a function of temperature is accounted for by an Arrhenius expression generally given as

$$k = k_0^{-E/RT}$$

For the case at hand, the rate parameters vary with temperature accordingly:

$$A = A_0^{-E/RT}$$

and

$$B = B_0^{-E/RT}$$

and so on, where T is in K, E is the activation energy term in kJ/gmol, and R is the gas constant. Seyfert's evaluation of these terms is given in Table 1. The intrinsic rate of reaction may thus be calculated for synthesis gases containing over 4% CO<sub>2</sub>.

The actual or observed rate of reaction, however, is a function of the degree to which diffusion limitations exist, and thus one can define the observed rate of reaction,  $R_{\text{obs}} = R_{\text{kin}}\eta$ , where  $\eta$  = the effectiveness factor. Said another way, the effectiveness factor  $\eta$  is defined as "the ratio of the observed rate of reaction to that which would occur in the absence of diffusion effects within the pores of the catalyst" [8]. Hasberg et al. [10] suggested that a value of  $\eta = 0.7$  may be reasonable for 5 × 5 mm pellets. With larger diameter catalyst particles, the effectiveness factor would rapidly decrease.

Table 1 Kinetic Parameters for Methanol Synthesis Reaction

Parameter	$k_0$	E (kJ/mol)
A	0.166	33.2
B	$2.16 \times 10^{14}$	148
C	$2.1 \times 10^5$	51.4
D	$1.21 \times 10^5$	45.3
E	$1.82 \times 10^8$	98
F	$1.83 \times 10^5$	60.4

Source: From Reference 9.

Actual sizing of commercial converters becomes an even more complex matter. The converter design itself has a marked bearing on the catalyst requirements depending upon the choice of a multibed intercooled, multibed quench, or isothermal converter. In addition to considering kinetic effects as given in the preceding discussion, some allowance is generally made for catalyst aging. By reducing expected activity to some minimum desired "end-of-run" performance criterion, a design activity is arrived at for use in sizing a commercial converter. Additionally, there may or may not be some additional allowance made for protecting the design volume of catalyst. This allowance or guard volume is estimated based upon some reasonable expectation of what concentrations of poisons, such as sulfur or chlorine, would be in the feed gas to the methanol synthesis loop. These points are considered differently from designer to designer: there is always a trade-off to be made between capital cost and long-term operability.

### 3.2.4

#### Effect of Operating Variables on Methanol Synthesis

##### 3.2.4.1

##### Temperature

The catalyst operating temperature has a marked effect on the rate of methanol synthesis. New converter charges of Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst should be operated as cool as possible at the inlet to preserve long-term life but generally not below 200°C. When equilibrium is not being achieved, an increase in the catalyst operating temperature gives a marked increase in methanol conversion. At design catalyst activity ("end of life"), a few degrees Celsius increase in the average bed temperature could result in a 35% increase in the rate of reaction and hence rate of methanol production. For a fresh catalyst, a 3°C increase in the average bed operating temperature could result in about a 10% increase in methanol production. However, as equilibrium is attained, further increases in temperature result in a reduction in the rate of methanol synthesis.

##### 3.2.4.2

##### Pressure

Pressure affects both equilibrium position and rate of reaction in methanol synthesis. From a total loop perspective, an increase (or decrease) in operating pressure affects more than merely the reaction conditions. It also affects the condensation of product (dew point) and recycle of methanol back to the converter system. Considering any given converter, however, calculations indicate that a 10% increase in operating pressure yields about a 10% increase in methanol production if equilibrium conditions exist. When the reaction is far from equilibrium and controlled by kinetics, the increase (or decrease) in methanol production is more than proportional to the increase (or decrease) in operating

pressure. A 10% increase in pressure under these conditions, for example, yields about a 20% increase in methanol production.

### 3.2.4.3

#### Circulation Rate

When the reactor system in methanol synthesis operates under kinetically controlled conditions, an increase in the circulating gas rate causes methanol production to decrease. If equilibrium is being achieved, however, one can expect that a 2.53% increase in production will be realized for a 5% increase in circulation and that a 56% increase in production will result from a 10% increase in circulation, and so forth.

### 3.2.4.4

#### H<sub>2</sub>/CO/CO<sub>2</sub> Concentration in the Loop

For a plant based upon a natural gas feedstock, the converter feed gas may have a composition roughly as that shown in Table 2. Small changes in loop gas composition should not have large effects on equilibrium, but depending upon the model one uses, the effect of synthesis kinetics may be more marked. Earlier models were heavily dependent upon hydrogen concentration; however, the more recently postulated models give more credence to the effects of carbon oxides. If one bases observations on variability in gas composition on the aforementioned converter system feed (which is high in hydrogen concentration and relatively low in CO/CO<sub>2</sub> concentration) and considers one of the more contemporary reaction rate models, one finds the following.

A 1% increase in hydrogen concentration results in a 4% decrease in carbon oxide content and causes expected production to drop by about 1%. With a 2% increase in hydrogen concentration accompanied by a 7+% decrease in carbon oxide content, methanol production under kinetically controlled conditions drops by more than 2%. At the relative low concentrations of carbon oxides

Table 2 Typical Composition of Feed Gas

Component	Mol%
H <sub>2</sub>	78.7
CO	4.33
CO <sub>2</sub>	3.48
Methanol	0.31
CH <sub>4</sub>	12.29
N <sub>2</sub>	0.85
H <sub>2</sub> O	0.04

observed in the feed gas under given conditions, small decreases in the carbon oxide content seem immediately to affect production. Alternatively, as hydrogen concentration is slightly decreased (say, 1% and then 2%) with total carbon oxides increasing by 4 and 8%, respectively, production is expected to increase under kinetically controlled conditions by about 1 and 2%, respectively.

### 3.2.5

#### Alternative Methanol Synthesis Loop Designs

As previously discussed, several converter designs are commercially available from various technology suppliers. All these different designs are generally incorporated into a synthesis loop, however, where fresh feed gas plus recycle is recirculated over the converter system. Because of the relatively low equilibrium constant with respect to methanol synthesis, recirculation is required to achieve reasonable yields on feedstock. Figure 1 displays a Kellogg synthesis loop that utilizes a series of adiabatic, intercooled spherical reactors. In this loop, fresh makeup gas (containing  $H_2$ , CO,  $CO_2$ , and some inert components, such as  $CH_4$  and  $N_2$ ) is blended with recycle gas on the discharge side of a single-stage recycle compressor. The fresh feed + recycle is preheated to reaction temperature in a shell-and-tube feed effluent exchanger before passing into the first reactor vessel. Note that a steam-heated start-up heater has been provided for catalyst reduction and initial loop start-up. This exchanger is not required during normal operations.

Reaction proceeds over the first bed adiabatically, the effluent being cooled indirectly by an intercooler that raises intermediate-pressure steam. The second, third, and fourth reactors operate in a similar manner, final reactor effluent being cooled in the feed-effluent exchanger. Methanol concentration in the effluent from bed 4 is typically about 5%. The effluent, once cooled in the feed-effluent exchanger, then passes to a crude condenser, where methanol and water of reaction are condensed out of the circulating gas. Typically this is a water-cooled exchanger, although air-cooled exchangers have had some application in this service. The condensed crude methanol is separated from the recirculating gas in a centrifugal separator. Recovered crude product then passes to the distillation train, where specification-grade product is produced. Recycle gas exiting the separator then returns to the suction side of the recycle compressor.

Between the crude separator and the recycle compressor, a purge is typically taken to control buildup of inerts and any excess reactants that may be present in the synthesis loop. Typically in natural gas-based plants, there is a large excess of hydrogen, which is removed from the loop at this point. Purge gas is generally used as supplementary fuel elsewhere in the battery limits plant, such as fuel to the fired reformer. Ratios of recycle to fresh feed are typically in the range

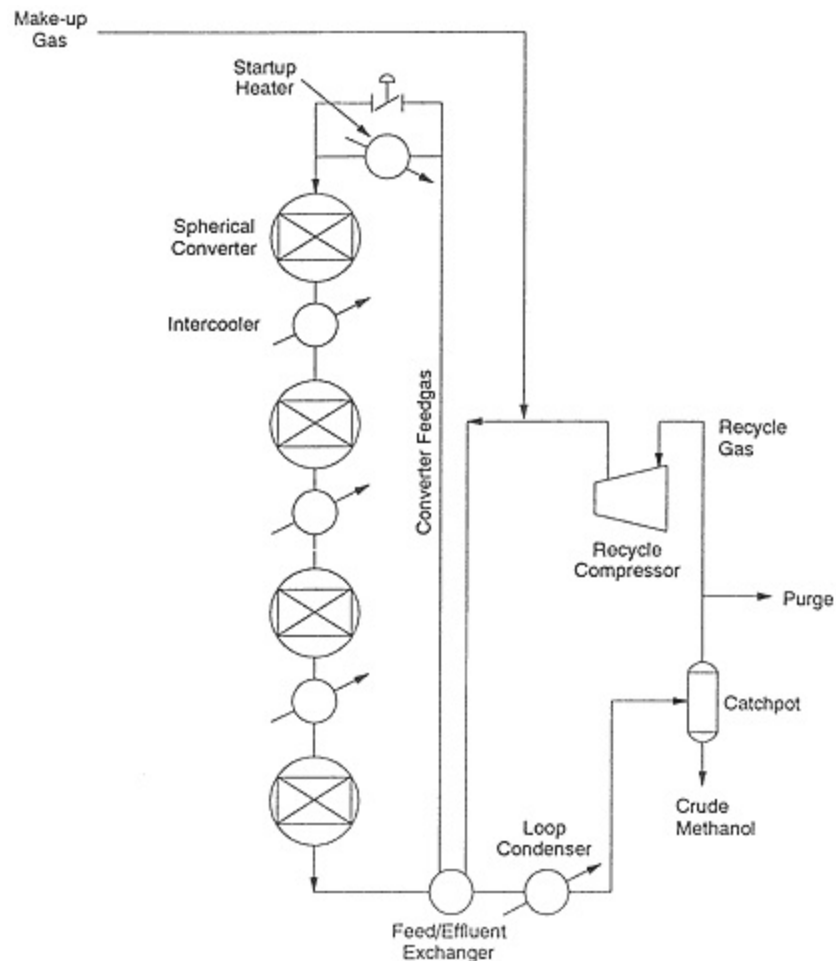


Figure 1

Methanol synthesis loop utilizing Kellogg spherical intercooled reactors.  
(Diagram courtesy of The M. W. Kellogg Company.)

34. The Kellogg spherical reactor system (see Fig. 2) has been successfully used in the Cape Horn methanol plant located near Punta Arenas, Chile.

Figure 3 [11] displays the classic ICI quench converter. A typical installation is shown in Figure 4. This design was the first to be used in low-pressure methanol synthesis plants and has been successfully applied in many instances. The loop that contains the ICI quench reactor is not very different from that given

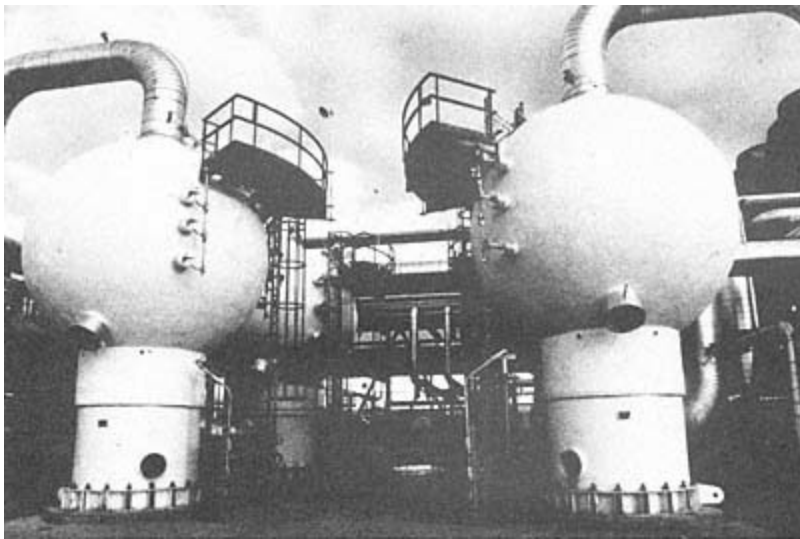


Figure 2  
Spherical reactors at Cape Horn Methanol (Cabo Negro, Chile).  
(Photograph courtesy of The M. W. Kellogg Company.)

in Figure 1 except that several beds are contained (generally) in a single converter, with interbed cooling accomplished via quenching with fresh feed. The converter displayed in Figure 3 is a four-bed unit. Part of the feed gas enters the top bed, and the remainder is used as interbed quench. This quench gas is introduced via distribution lozenges, as indicated by points C in the figure. Figure 5 [11] displays the reaction path for the quench converter. Note that the concentration of methanol in the gas exiting any given bed (except the last bed) is diluted somewhat by the direct-quench cooling process. This diagram also indicates what the path might be for an intercooled design, in which interbed dilution is not a factor. Note that in the ICI design, heat of reaction is recovered at the exit of the converter. Recovered heat is used typically to heat high-pressure boiler feedwater, reformer feed saturation circulating water, and, finally, fresh reactor feed. ICI also more recently offered a new converter design, the tube-cooled converter. Figure 6 [11] displays this particular design. In the tube-cooled design, reaction gas temperature is controlled by transferring heat to the incoming feed on the inside of the tubes.

At least two commercial isothermal designs are also available. Figure 7 [12] displays a typical Lürgi tubular converter arrangement. The Lürgi isothermal converter is a shell-and-tube unit in which catalyst is contained within relative-

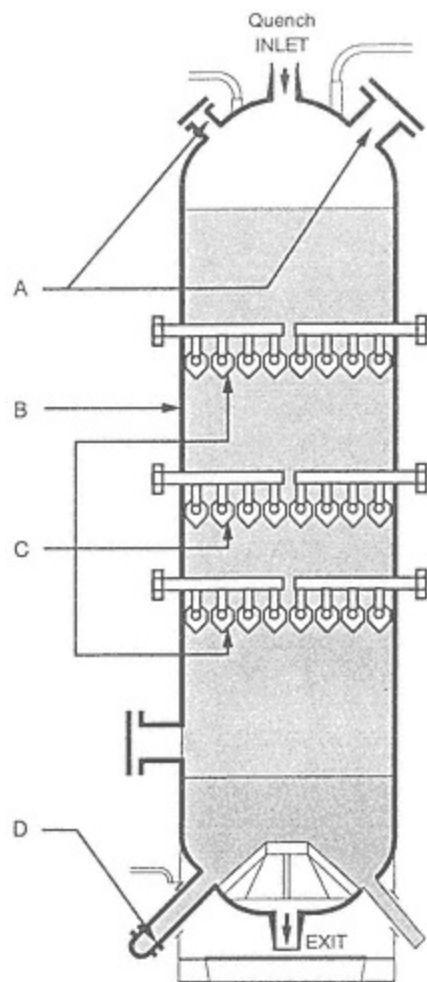


Figure 3

Typical ICI quench converter.

(A) Catalyst is charged and inspected through these ports.

(B) The pressure vessel is of a simple design no internal catalyst basket is required.

(C) The ICI lozenge quench distributors ensure good gas distribution and allow the free passage of catalyst for charging and discharging.

(D) Gravity discharge of catalyst permits rapid preparation for maintenance or recharging.

(Diagram courtesy of ICI.)



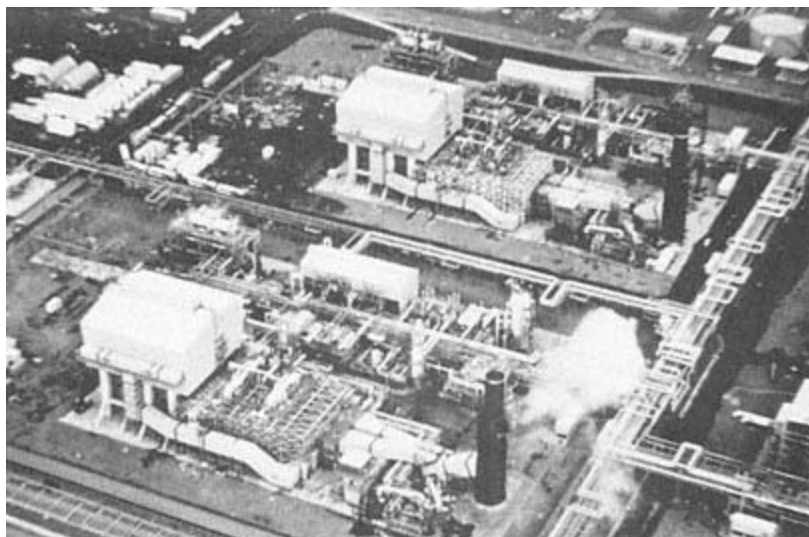


Figure 4  
Twin 2200 tpd methanol units at Methanex Corporation, Motunui, New Zealand.  
(Photograph courtesy of ICI.)

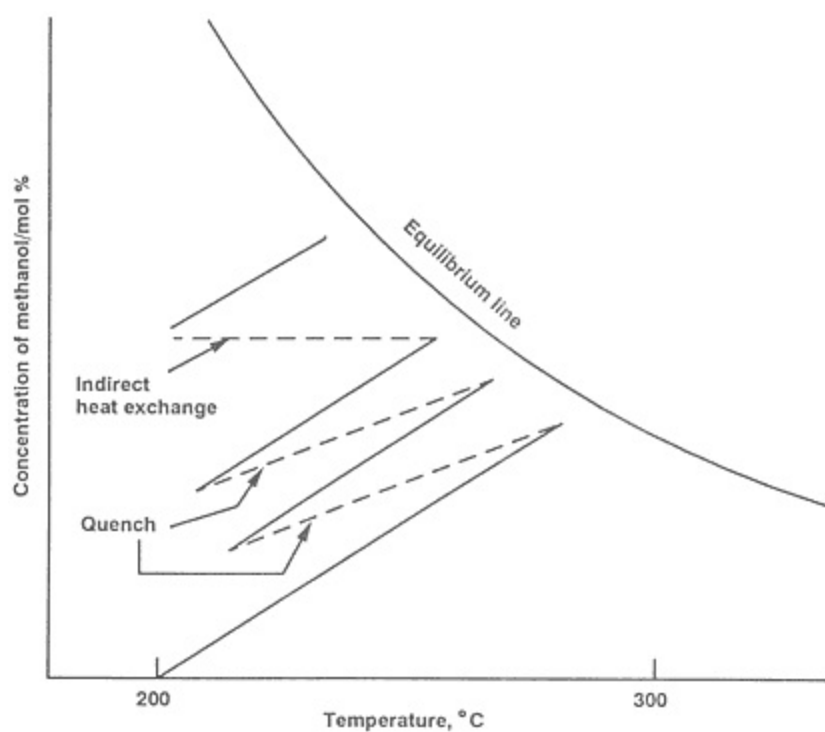


Figure 5  
Temperature concentration profiles for a quench converter and an intercooled converter. Inlet temperature 200°C, exit temperature 240°C.  
(Diagram courtesy of ICI.)

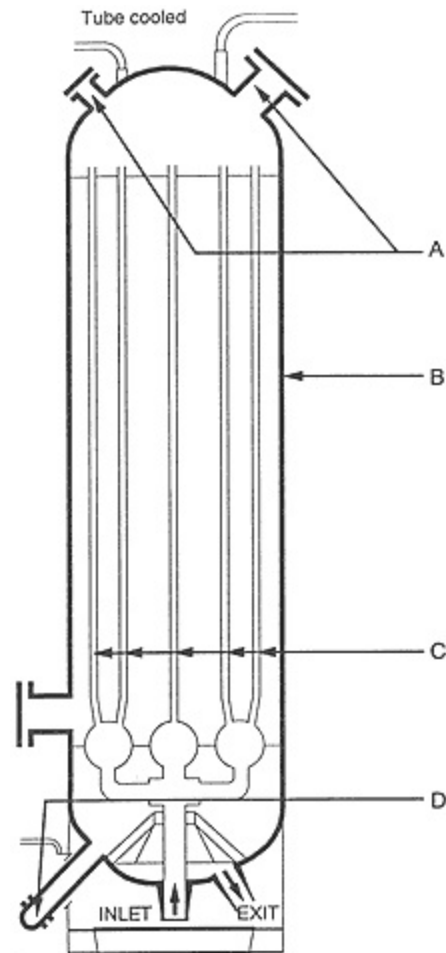


Figure 6

ICI tube-cooled converter.

(A) Catalyst is charged and inspected through these ports.

(B) The pressure vessel is of a simple design no internal catalyst basket is required.

(C) Thin-walled cooling tubes are welded to a simple header system embedded in the catalyst.

(D) Gravity discharge of catalyst permits rapid preparation for maintenance or recharging.

(Diagram courtesy of ICI.)

ly small diameter tubes. Reaction heat is transferred to the shell side, which contains boiling water. The shell side is connected to a steam drum, where nominally 4 MPa (40 atm) steam is raised. In the diagram one converter is shown, but several Lurgi installations have used a dual-converter system. The decision regarding the use of one or two converters is mostly dependent upon

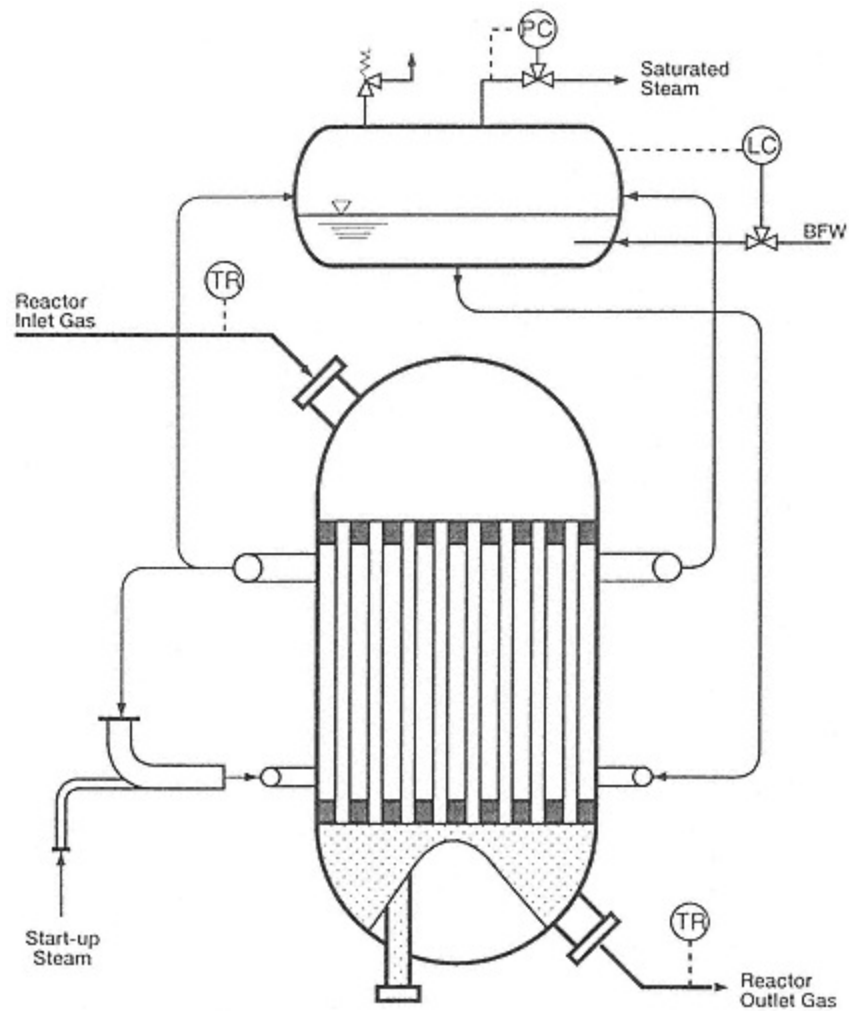


Figure 7  
 Typical Lürgi tubular methanol converter arrangement.  
 (Diagram courtesy of Lürgi GmbH.)

desired plant capacity. Figure 8 [12] displays a plot of reactor temperature versus tube length for the Lürgi isothermal converter. The various curves refer to different points in the life of the catalyst (aged versus new). Note the rapid increase in temperature in the top of the tubes as the feed gas is heated to reaction tem-

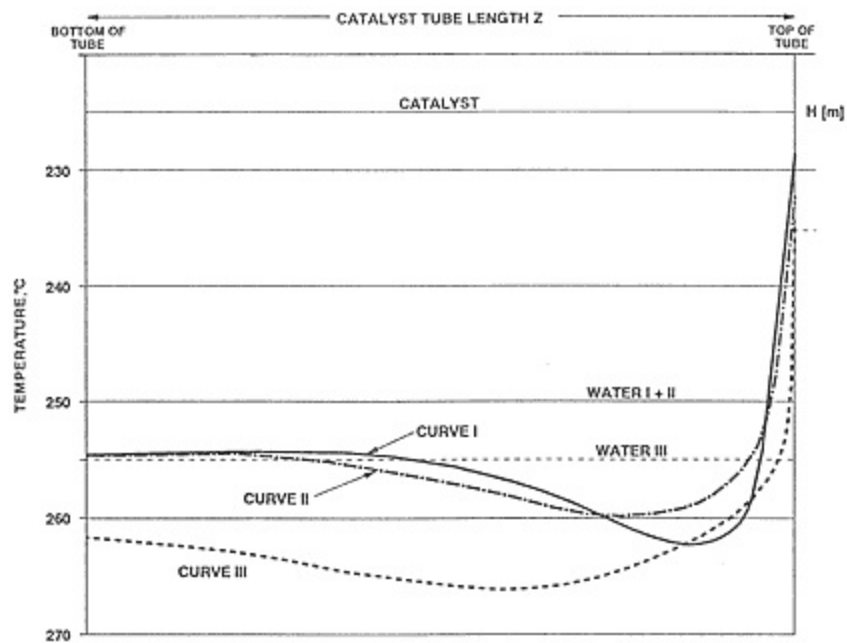


Figure 8  
 Reactor temperature versus tube length for the Lürgi isothermal converter.  
 Curves I, II, and III denote behavior of catalyst as a function of age.  
 (Diagram courtesy of Lürgi GmbH.)

perature. Once the peak has been reached, there is a slight drop in temperature, which is at a fairly constant offset from the equilibrium temperature. This operation is often referred to as "quasi-isothermal." Reactor effluent from the Lürgi converter system typically contains about 68% methanol. Some 26 commercial Lürgi methanol reactors with a total capacity of about 20,000 t/day have been built as of 1993. Figure 9 displays the 1200 t/day Lürgi methanol reactor installed at Wesseling, Germany.

Another isothermal design is offered by Linde of Germany. Figure 10 [13] displays a cutaway diagram of this converter. In the Linde converter, unlike the Lürgi unit, the process gas is on the shell side and water boils in the tubes, which are embedded within the catalyst zone in a helical arrangement. An integral steam drum is connected to the helix tubes, which make up the risers and downcomers from which steam is generated within the converter. As with the Lürgi unit, the isothermal reactor may be controlled by varying the steam drum pressure. At higher drum pressures, the catalyst bed operates hotter; at lower pressures, it

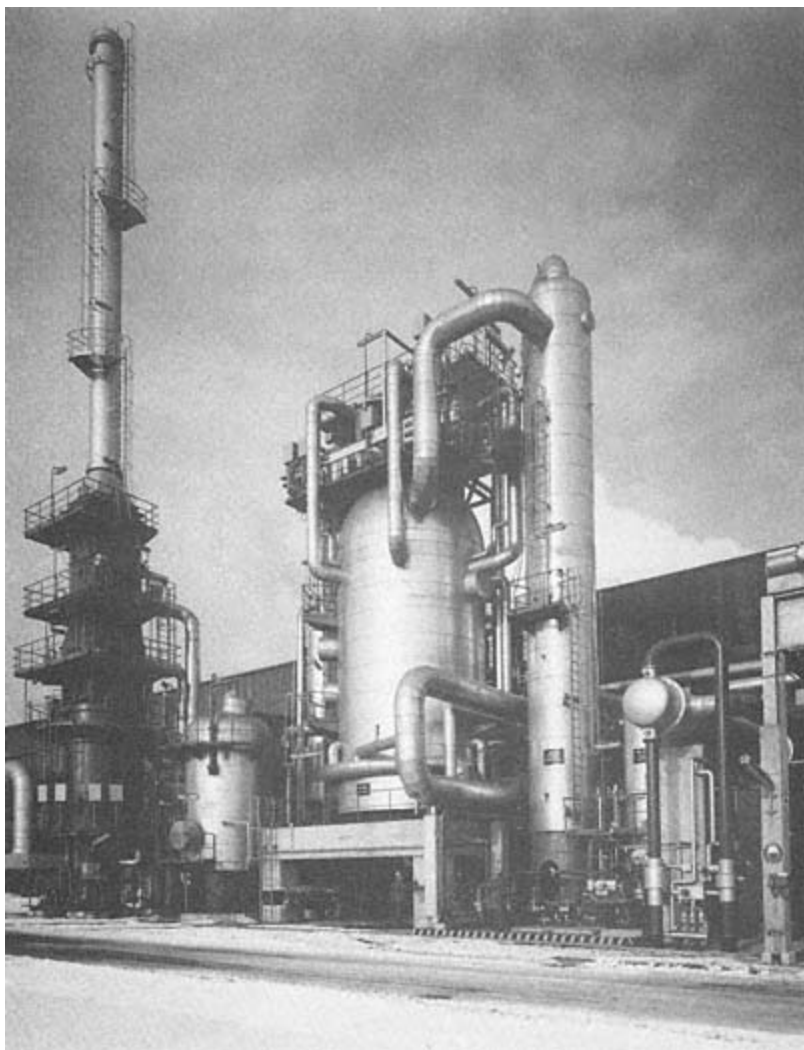


Figure 9  
Lürgi converter installation at Wesseling, Germany.  
(Photograph courtesy of Lürgi GmbH.)

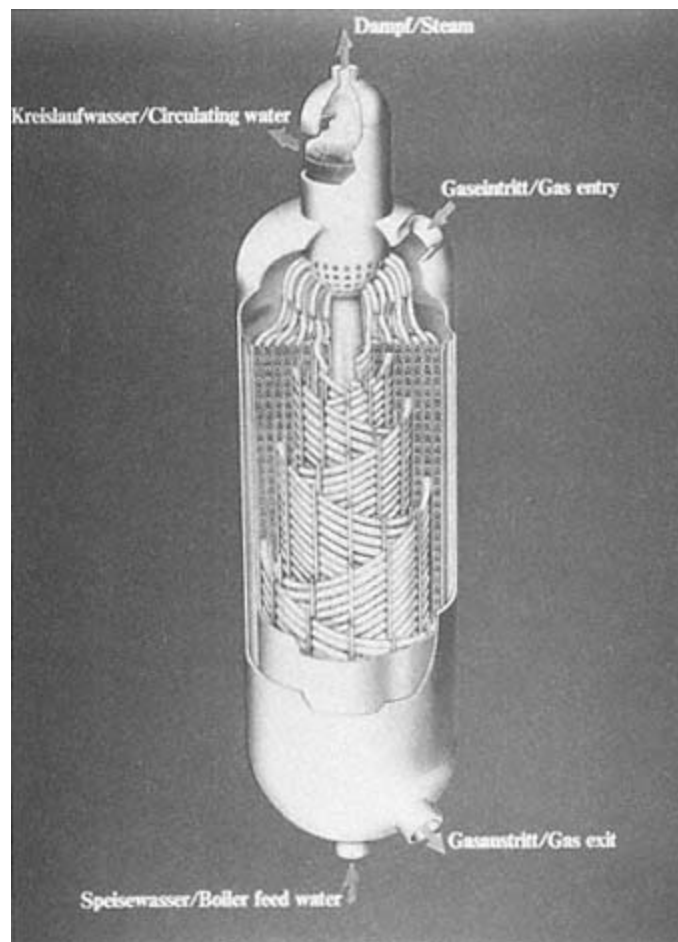


Figure 10  
A Linde spiral-wound converter.  
(Diagram courtesy of Linde AG.)

operates cooler. Typically, one expects to increase the converter temperature as the catalyst begins to show signs of aging. The Linde converter has been successfully applied to commercial methanol facilities, perhaps the most notable of which is the BASF plant at Ludwigshafen, Germany. A photograph of this installation is displayed in Figure 11.

Other gas-phase methanol synthesis converter designs are available from such designers as Haldor-Topsøe and Mitsubishi Gas Chemical Company.

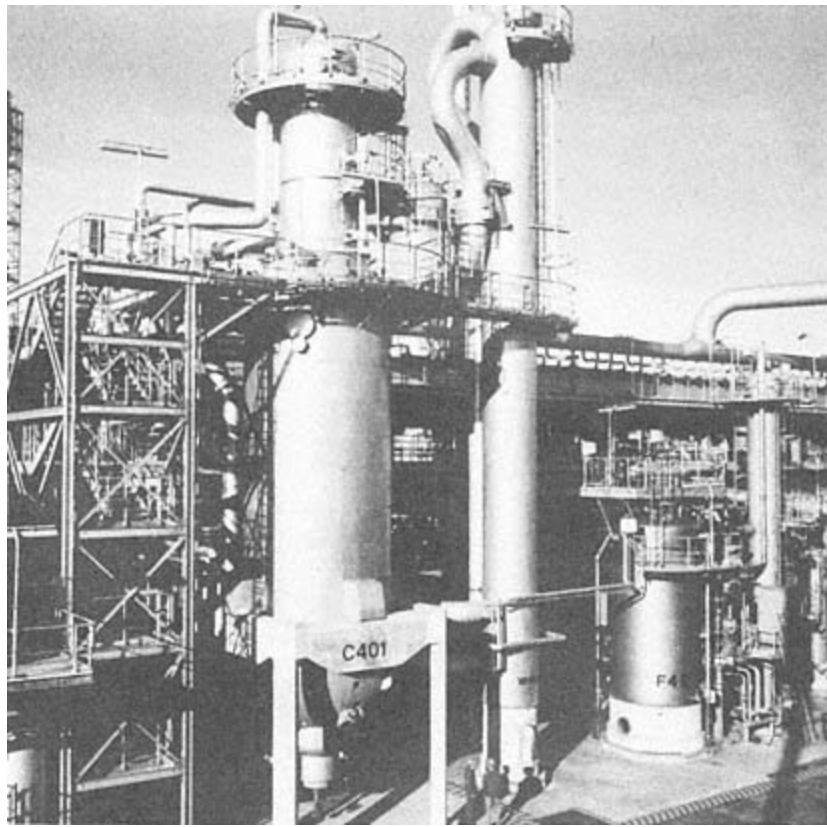


Figure 11

Linde converter installation at the BASF Ludwigshafen works.  
(Photograph courtesy of Linde AG.)

### 3.2.6 Catalyst Yield Factors

The various designs for gas-phase methanol synthesis have their own peculiarities along with associated advantages and disadvantages. Because of variations in approach to equilibrium and catalyst utilization, each of the systems previously described exhibits different yield factors with respect to the required volume of methanol synthesis catalyst. Traditionally, the isothermal converters have required the lowest catalyst volumes because of the more or less constant approach to equilibrium achieved as the gas passes downward through the catalyst-filled tubes. This reactor then exploits the maximum reaction rate by ap-



proaching without quite reaching the equilibrium point. Isothermal converters typically are designed with a yield factor in the general neighborhood of 0.91.0 kg methanol/h/L catalyst.

Quench converters have typically exhibited the largest installed catalyst volumes per ton of methanol produced and therefore have the lowest yield factor. A quench converter is normally expected to be designed for a yield of 0.350.40 kg methanol/h/L catalyst.

Adiabatic intercooled converters fall between quench converters and isothermal converters. They exhibit the so-called sawtooth reaction profile as observed in a quench converter. However, all the gas passes through all the catalyst, which allows a significant improvement in catalyst utilization. This concept was adopted long ago in the ammonia industry: most modern ammonia converters are intercooled rather than quench. The adiabatic-intercooled converter is typically designed with a yield factor of approximately 0.550.60 kg methanol/h/L catalyst.

### 3.2.7

#### Liquid-Phase Processes

Significant development has occurred within the industry over the last several years with respect to liquid-phase processes. One example of this process that is reasonably close to commercialization is that developed by Air Products. A pilot unit has been operated for several years at their La Porte, Texas location. The process is characterized briefly as using an inert hydrocarbon reaction medium in the liquid phase to absorb the synthesis heat of reaction; conventional copper-zinc catalyst is fed to the reactor system as a slurry. This type of process appears to be particularly well suited to substoichiometric feeds (high carbon content), such as those produced by partial oxidation or coal gasification. The Air Products process has been extensively described in patent literature [14]. Kinetic data and liquid-phase reaction systems have also been extensively discussed by Lee in Methanol Synthesis Technology [15].

### 3.3

#### Syngas Preparation Processes

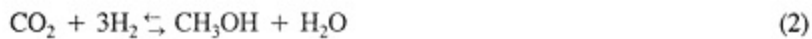
As discussed in Section 3.2, methanol may be synthesized from a gas containing  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$  in varying proportions, which depend mostly on the feedstock of choice. The syngas from which methanol is ultimately produced may come from any number of different routes, including coal gasification, partial oxidation of heavy oils, steam reforming of natural gas (with or without  $\text{CO}_2$  injection), steam reforming of LPG feedstocks and naphthas, combined or oxygen-enhanced reforming, and heat-exchange reforming. This list names the principal routes by which methanol synthesis gas may be produced.



Recalling that methanol may be produced by the following reactions:



and



the degree to which the syngas is stoichiometric may be determined by the stoichiometric ratio  $R$ ,

$$R = \frac{\text{moles H}_2}{2 \times \text{moles CO} + 3 \times \text{moles CO}_2}$$

A balanced or stoichiometric syngas has an  $R$  value close to unity. Substoichiometric gases have  $R$  values less than unity, and  $\text{H}_2$ -rich gases (sometimes referred to as low-carbon gases) have  $R$  values that are greater than unity. Steam reforming of methane, for example, yields a syngas that typically has an  $R$  value of about 1.4 because of the  $\text{H}/\text{C}$  ratio of the feedstock. Reforming of feeds with lower  $\text{H}/\text{C}$  ratios (such as propane, butane, or naphthas) yields syngases with  $R$  values closer to stoichiometric. Sometimes, the stoichiometric nature of the feed is referred to in a different manner. The stoichiometric number  $S$  has been defined as

$$S = \frac{\text{moles H}_2 - \text{moles CO}_2}{\text{moles CO} + \text{moles CO}_2}$$

$S$  values of approximately 2.0 are representative of stoichiometric syngases.  $\text{H}_2$ -rich syngases have  $S$  values that are greater than 2.0.

All the aforementioned front-end process routes exhibit varying efficiencies, capital costs, and operating complexities. No single route is best, but a particular route is likely to be best under certain project- and/or site-specific circumstances. Project specifics generally dictate the preferred synthesis gas generation route. In this section, each of these routes is reviewed briefly for purposes of comparison.

### 3.3.1

#### Coal Gasification

Coal gasification is accomplished by a combination of partial oxidation and hydrogasification of coal feedstock according to the following chemical reactions:





Low Btu value gas is typically produced when air is used as the oxidant. The heating value improves markedly when pure oxygen is substituted for air.

Coal gasification has been expected for many years to become the preferred route for syngas generation in the United States because of large indigenous coal reserves; however, given the continued availability of natural gas and the higher cost of coal conversion, the boom in coal as a chemical feedstock has yet to come. Significant development work in this area continues nonetheless, and several designs have been successfully commercialized.

Several different types of gasification units have been developed over the years. These include moving- or fixed-bed gasifiers, fluidized-bed gasifiers, entrained-flow gasifiers, and those based upon the molten-batch process.

Commercial gasification units include the Koppers-Totzek entrained-flow atmospheric gasifier, the Winkler fluidized-bed atmospheric gasifier, the Lürgi fixed-bed pressurized gasifier, and the Texaco pressurized entrained-flow gasifier. Table 1 in the Kirk-Othmer Encyclopedia of Chemical Technology [16] gives a listing of gasification unit types that are either already commercialized or in development.

The properties of a particular coal play a significant role in the ultimate selection and design of the gasification equipment. Some of the more important coal properties that bear careful consideration include moisture content, ash content, volatile content, fixed carbon availability, caking behavior, reactivity, and particle size distribution. Ash content and reactivity are properties that are somewhat tied together in that the inorganic impurity content of the coal can play a significant role in the rate of reaction between hydrogen, carbon dioxide, steam, and oxygen. This is because of the catalytic effect imparted by the presence of impurities, such as potassium and iron.

The Koppers-Totzek (K-T) gasifier produces a medium-Btu gas (in the general range of 300 Btu/scf) and has been commercially employed in many different syngas applications, with particular emphasis in the area of ammonia synthesis. The process is carried out at just over atmospheric pressure but at very high temperatures of over 1870°C. The data in Table 3 [16] give the expected K-T gasifier product composition for an Illinois coal (62% C, 19.1% ash, 4.4% H<sub>2</sub>, and 5% S plus O<sub>2</sub> and H<sub>2</sub>O) that has been gasified with a steam-coal ratio (wt/wt) of 0.27 and an oxygen/coal ratio (wt/wt) of 0.7. K-T units vary in size between those that convert about 300 t coal per day and those that convert over 750 t coal per day.

Table 3 Raw Gas Analysis of Products from a K-T Gasifier

CO	55.4%
CO <sub>2</sub>	7.1%
H <sub>2</sub>	34.6%
N <sub>2</sub>	1.0%
H <sub>2</sub> S	1.8%
COS	0.1%
Heating value	290 Btu/scf
Gas make	60,000 scf/ST
Coal to gas efficiency	Approximately 76%

The Lürgi pressurized gasifier has been used extensively in commercial applications for Fischer-Tropsch syngas generation and Synthetic Natural Gas applications in which CO/H<sub>2</sub> gas is converted to a high-Btu gas via methanation within the gasifier as well as in downstream reactors (methane formed via  $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ ).

The Lürgi gasifier is depicted schematically in Figure 12 [16]. The unit is designed to operate at pressures of up to 3.2 MPa (32 atm). Coal is fed through a top-mounted lock hopper to a bed within the body of the gasifier. The bed is uniformly fed by the rotating distributor as shown. Steam and oxygen are sparged through a revolving gate, where ash is removed to a bottom-mounted lock hopper for eventual discharge from the unit. Gas discharges from the unit at temperatures of up to 600°C. The process conditions and gas composition depend largely on the type of coal feed employed. Table 4 [16] compares gasification product gases achieved with a variety of coal feed types for a Lürgi pressurized gasifi-

Table 4 Product Gases from Gasification of Different Coals for a Lürgi Gasifier

Component (vol%)	Lignite	Subbituminous coal	Low volatile coal
CO <sub>2</sub>	31.9	28.2	26.5
CnHm	0.5	0.3	0.1
CO	17.4	20.6	21.4
H <sub>2</sub>	36.4	39.6	43.5
CH <sub>4</sub>	13.5	10.5	8.0
N <sub>2</sub>	0.3	0.8	0.5
Approximate heating value, Btu/scf	325	304	290

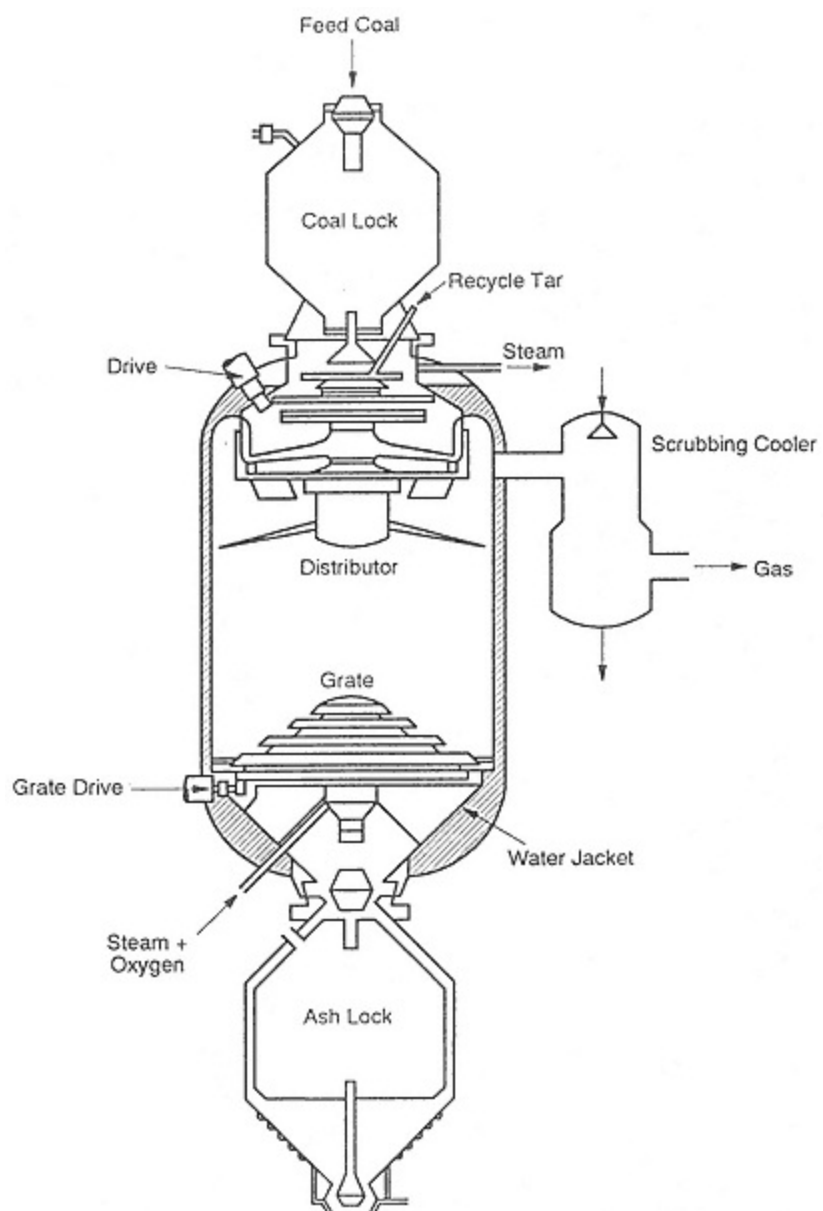


Figure 12  
Lurgi coal gasifier.  
(Diagram courtesy of Lurgi GmbH.)

er. Product gas from a Lürgi gasifier is typified by a higher than average methane plus higher hydrocarbon content compared with gasifiers that operate at lower pressure and higher temperatures. Lürgi, together with British Gas Corporation, has developed but not yet commercialized a slagging version of their original gasifier that reportedly features a higher specific throughput at a much lower steam consumption.

Texaco has successfully commercialized a pressurized gasification reactor that is of the entrained-flow type. Figure 13 [17] displays a schematic diagram for the Texaco coal gasification process. This process operates at pressures of about 3.8 MPa (38 atm) and a temperature in the range of 1450°C. The gasifier operating temperature is typically a function of the coal feed properties. The coal feed is pumped into the unit as an approximately 60% slurry. Table 5 [17] gives

Table 5 Representative Operation Data for a Texaco Gasifier

Coal composition	
Volatile matter, wt%	25.4
Fixed carbon, wt%	55
Moisture, wt%	8.0
Ash, wt%	11.6
Carbon, wt% (dry and ash free)	86.1
H <sub>2</sub> , wt%	5.0
O <sub>2</sub> , wt%	5.8
N <sub>2</sub> , wt%	1.7
S, wt%	1.2
Operating pressure, atm	38.4
Operating temperature, °C	1450
Crude gas composition	
Product gas, dry mol%	
CO <sub>2</sub>	13.5
CO	51.5
H <sub>2</sub>	34.3
CH <sub>4</sub>	0.05
C <sub>n</sub> H <sub>m</sub>	
N <sub>2</sub>	0.4
Crude gas yield stp, m <sup>3</sup> /t (dry and ash free)	2430
O <sub>2</sub> consumption, m <sup>3</sup> /m <sup>3</sup>	0.314
Cold gas efficiency, %	73.3
Carbon conversion, %	99

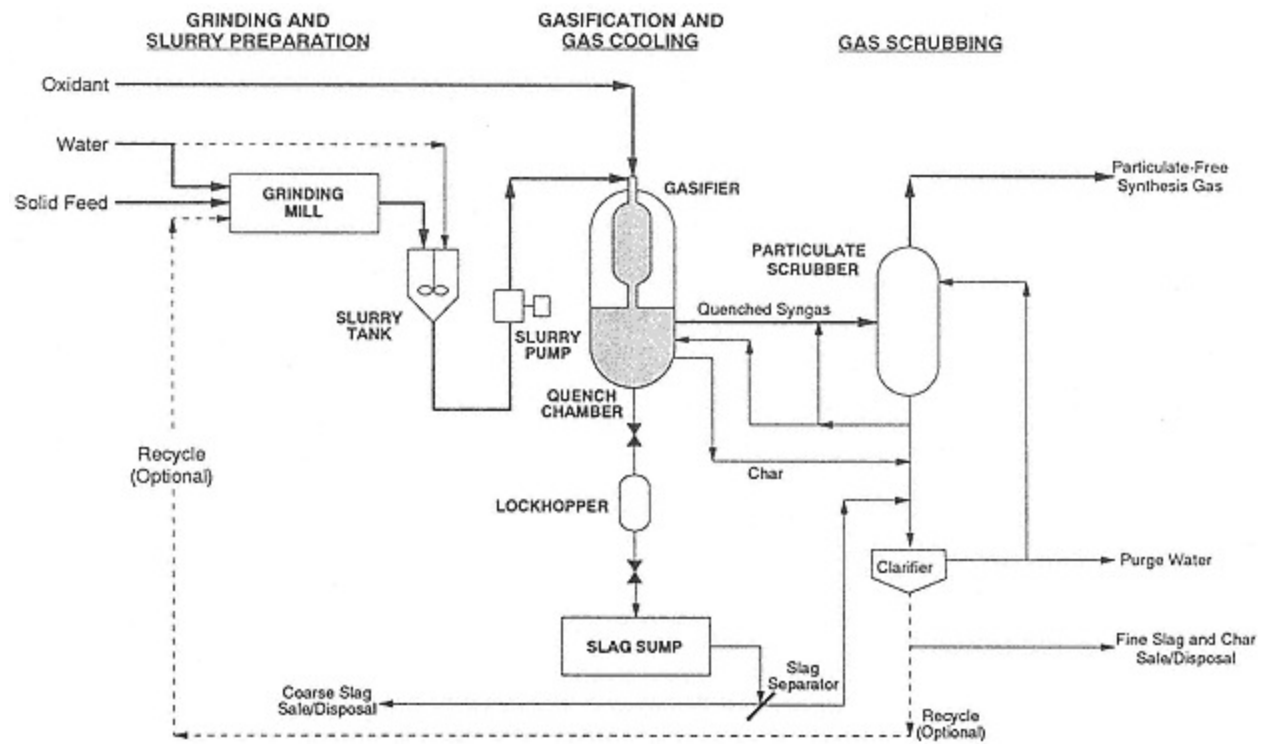


Figure 13  
Texaco coal gasifier operated in the quench mode.  
(Diagram courtesy of Texaco Development Corporation.)

representative data for a Texaco gasifier operating on a bituminous coal. For syngas conversion to methanol or ammonia, the process is preferably operated in the quench mode to promote downstream shifting of CO to H<sub>2</sub>.

For methanol synthesis, the raw gas leaving the gasification unit requires significant additional treatment. Once the gas has been cooled (generally in a direct contact scrubber in which particulate matter is also removed), COS is hydrolyzed over a suitable catalyst, H<sub>2</sub>S is removed to a large extent, the gas composition is shifted across a sour gas shift converter ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$  reaction promoted over a cobalt-molybdenum catalyst), and finally excess CO<sub>2</sub> is removed. The syngas is then ready for compression before passing into the methanol synthesis loop.

Syngas produced from coal gasification yields a raw gas that is very carbon rich and therefore substoichiometric ( $R < 1.0$ ). By shifting some of the CO to H<sub>2</sub> and subsequently removing excess CO<sub>2</sub>, a balanced or stoichiometric gas ( $R \cong 1.0$ ) can easily be achieved.

Worldwide, there have been more applications of coal gasification for ammonia synthesis than for methanol synthesis (particularly in China), although the process is appropriate for methanol. In the United States, Tennessee Eastman Corporation (Kingsport, Tennessee) has operated for several years a methanol-manufacturing facility based on Texaco coal gasification followed by a Lurgi-designed synthesis loop (utilizing their tubular isothermal converter design). The plant nominally produces 600 stpd of methanol.

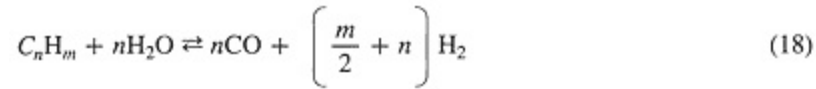
Coal gasification may likely find future application in methanol production for utilization in combined cycle power generation facilities. In this case, the methanol (stored on-site as a liquid) will be utilized as a peak shaving fuel and will be produced from excess gasifier capacity as power demand is reduced. Several different schemes have been proposed for combining methanol production with coal gasification in a power plant scenario. This particular arrangement may be most favorable for a liquid-phase process (see reference to the Air Product process in Sec. 3.2.7) that can utilize a substoichiometric feed with a reasonable once-through conversion while passing on unconverted gas to the combined cycle gas turbine as a fuel.

Coal gasification for application in methanol will be justified by today's economic criteria only in special cases. The cost of the methanol production unit will be no different from that based on other feeds, although the cost of the coal gasification unit is expected to be significantly greater than the cost of a comparably sized gas feed-based facility, such as a steam-methane reformer. Emphasis on coal as a methanol feedstock will undoubtedly grow at some later date when natural gas supplies are expected to be much less plentiful.

### 3.3.2

#### Partial Oxidation

The partial oxidation (POX) of heavy oils is a process whereby incomplete combustion of hydrocarbons is affected according to the following general chemical reactions:



The minimum amount required to achieve complete conversion of the hydrocarbon feedstock is 0.5 mol O<sub>2</sub> per mol carbon. Steam is added to control the reaction temperature, which leads to additional H<sub>2</sub> generation via CO shift [Eq. (3)]. The final partial oxidation effluent gas composition is governed by the following chemical equilibrium expressions:



Partial oxidation is achieved at reactor conditions ranging from 1350 to 1600°C and pressures of up to 15 MPa (150 atm). This process is attractive because it allows utilization of hydrocarbon feeds that could not be handled in the more conventional vapor-phase processes, such as steam reforming. Particular disadvantages of the process (besides the need to furnish pure oxygen for POX reactor injection) include cost and the inevitability of soot formation either via thermal cracking of the feedstock or through the Boudouard reaction (CO disproportionation),



Additionally, reactor effluent gas in partial oxidation always contains sulfur in the form of H<sub>2</sub>S and COS, which requires eventual downstream removal before the synthesis gas can be used for methanol manufacturing.



Successful commercialization of partial oxidation processes has been achieved by both Shell and Texaco. Figure 14 [17] displays a schematic of the Shell process, and Figure 15 [17] displays a schematic of the Texaco process. Both processes are similar. Commercial units based on Shell and Texaco partial oxidation processes (considered in total) number in the several hundreds.

Table 6 [17] gives some typical results from the partial oxidation of a vacuum residue with soot recirculation. The product gas from partial oxidation is not suitable for methanol synthesis because it is highly substoichiometric (carbon rich). Figure 16 is a block flow diagram describing the basic process steps required to adapt partial oxidation to methanol synthesis.

Once the raw gas has been scrubbed for soot removal,  $H_2S$  is removed and  $CO$  is shifted across a cobalt molybdenum sour gas shift catalyst to adjust the  $H_2O/CO/CO_2$  ratio. Finally, excess  $CO_2$  is removed and the gas may be compressed (if required) and then processed in a conventional methanol synthesis loop. The processing steps as just described yield a syngas that is approximately stoichiometric in nature ( $R \cong 1.0$ ) although considerably more concentrated in  $CO$  than  $CO_2$ .

Several commercial methanol production facilities have been constructed worldwide using partial oxidation as a source for synthesis gas.

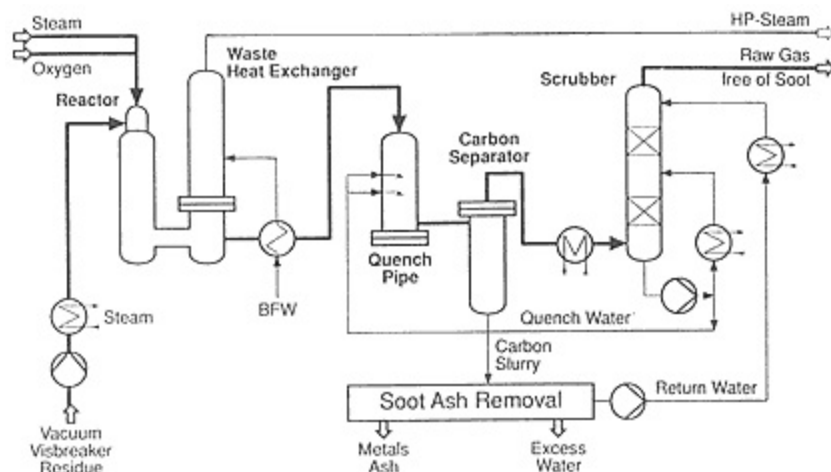


Figure 14  
Shell heavy oil partial oxidation unit.  
(Diagram courtesy of Lurgi GmbH.)

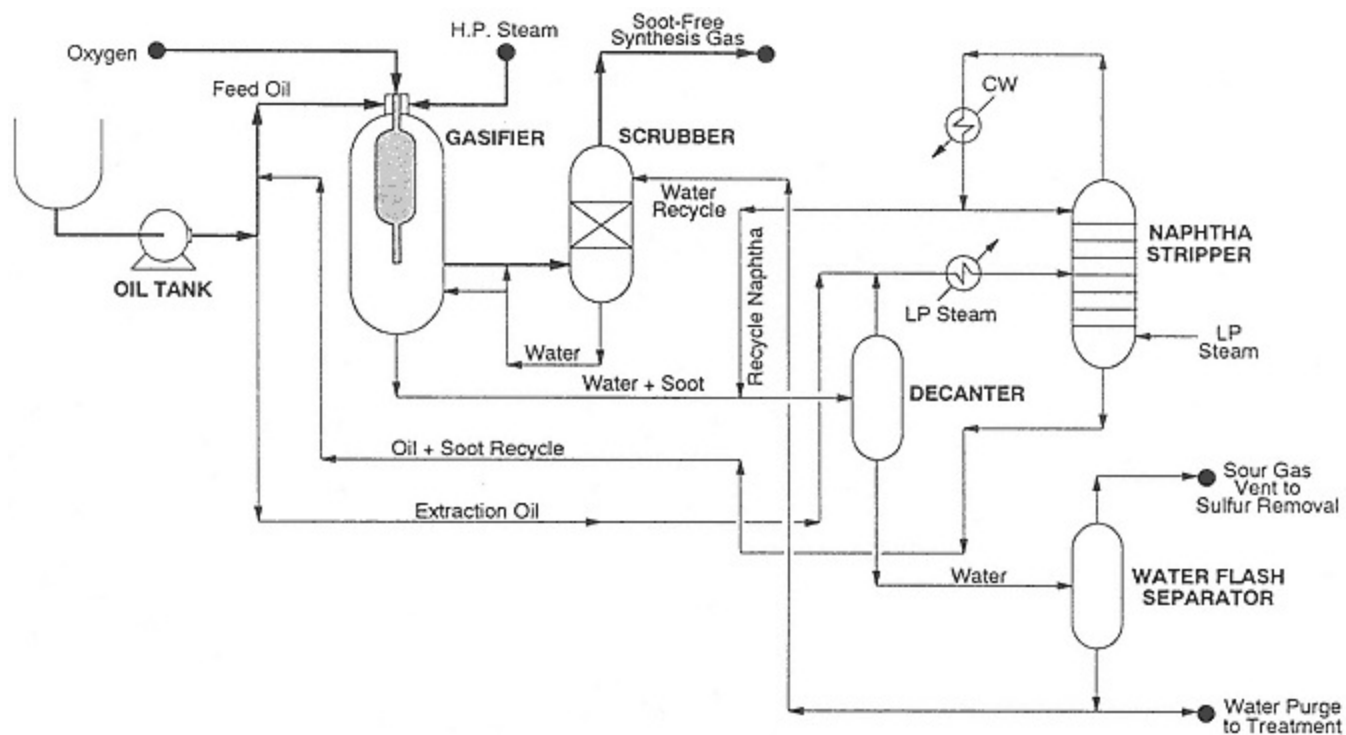


Figure 15  
Texaco heavy oil partial oxidation unit.  
(Diagram courtesy of Texaco Development Corporation.)

Table 6 Typical Operation of a Partial Oxidative Process

Operating pressure, MPa (atm)	5.9 (59)
Feedstock, kg	100
Pure O <sub>2</sub> , m <sup>3</sup>	70.7
Steam, kg	50
Product gas volume, m <sup>3</sup>	290
Gas composition, mol%	
CO <sub>2</sub>	4.63
CO	48.92
H <sub>2</sub>	44.94
CH <sub>4</sub>	0.3
N <sub>2</sub> + Ar	0.2
H <sub>2</sub> S + COS	1.01

### 3.3.3

#### Natural Gas Steam Reforming

For many years, the overwhelming feedstock of choice for methanol producers has been natural gas. As of 1990, some 75% of the world's methanol production capacity was based on a natural gas feedstock. Steam reforming with its low sulfur feed gas (typically, feeds to a reformer contain less than 0.1 ppmv total sulfur) makes synthesis gas that is particularly well suited to feed a loop containing Cu-Zn catalyst. With the advent of the low-pressure process (pressures of 10 MPa, 100 atm, or less), it became advantageous to feed gases to a loop that were not necessarily stoichiometric because of the overall reduction in compression requirements.

Consider the feedstock in the following table:

Component	Dry mol%
CO <sub>2</sub>	1.75
N <sub>2</sub>	0.40
C <sub>1</sub>	82.62
C <sub>2</sub>	8.56
C <sub>3</sub>	3.82
i-C <sub>4</sub>	0.78
n-C <sub>4</sub>	1.15
i-C <sub>5</sub>	0.30
n-C <sub>5</sub>	0.27
C <sub>6</sub>	0.22
C <sub>7</sub>	0.10
C <sub>8</sub>	0.03
C <sub>9</sub>	0.01
Total	100.0

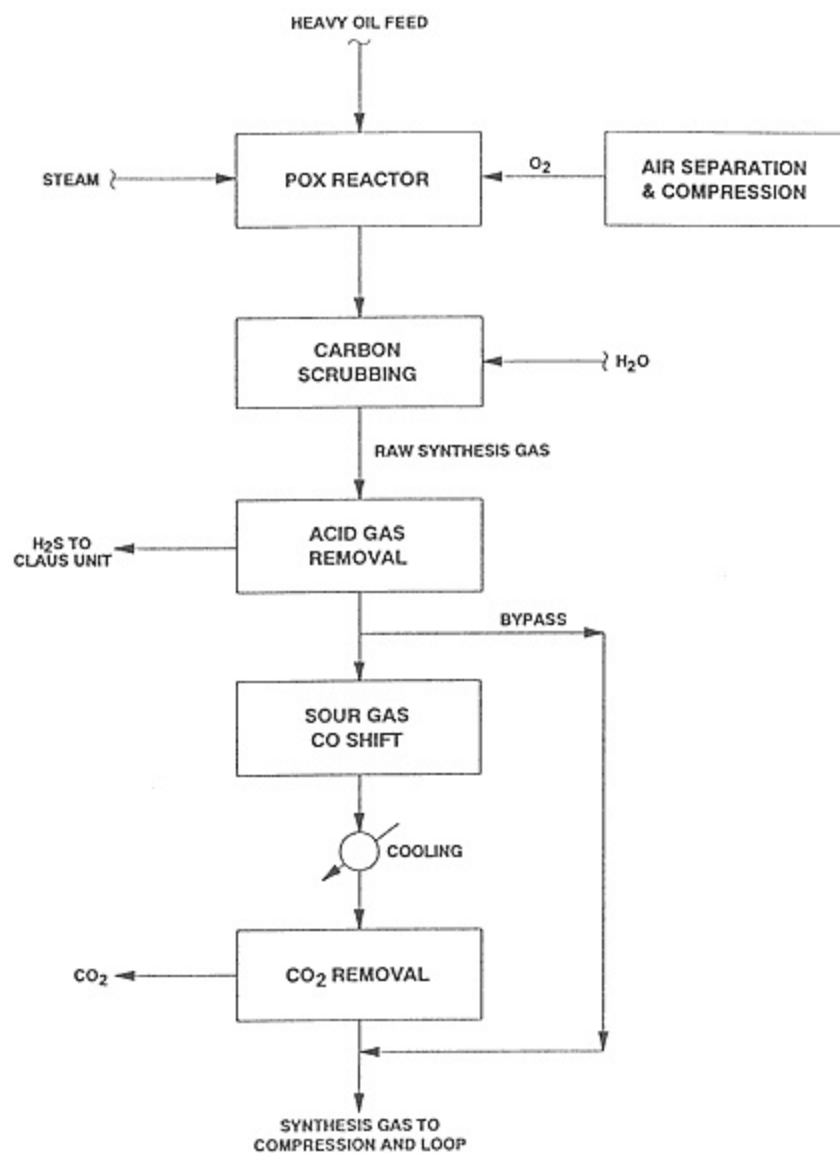
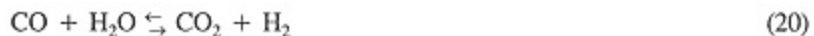


Figure 16  
Partial oxidation.

This feedstock, although perhaps slightly heavier than a typical U.S. Gulf Coast natural gas (because of C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub><sup>+</sup> content) is easily steam reformed over a conventional nickel-on-alumina catalyst at normal steam ratios. Syngas generation proceeds according to the following reactions:



and



From these equations it is apparent that, theoretically, one can produce 4 mol hydrogen for every mol methane fed to the reformer. Since methanol may be produced as follows:



Summing Equations (26) and (2) gives



Thus it is apparent that a methane-rich natural gas feedstock yields a hydrogen-rich or low-carbon synthesis gas.

The natural gas given in the preceding table, when reformed at a catalyst exit temperature of 860°C, a pressure of 2 MPa (20 atm), and a steam-carbon ratio of 3:1, yields a syngas with the following composition:

Component	Dry mol%
H <sub>2</sub>	72.10
N <sub>2</sub>	0.09
CH <sub>4</sub>	4.26
CO	14.75
CO <sub>2</sub>	8.80

The stoichiometric ratio  $R [\text{H}_2/(2\text{CO} + 3\text{CO}_2)]$  for this particular syngas may be calculated to be approximately 1.3, which is expected. Normally in steam reforming of a natural gas feedstock,  $R$  values of 1.3-1.4 are observed. Lower steam ratios of about 2.7-2.8 are possible, some overall energy benefits being achieved at these lower ratios, but operating at values much below this level has generally not been found to be prudent.

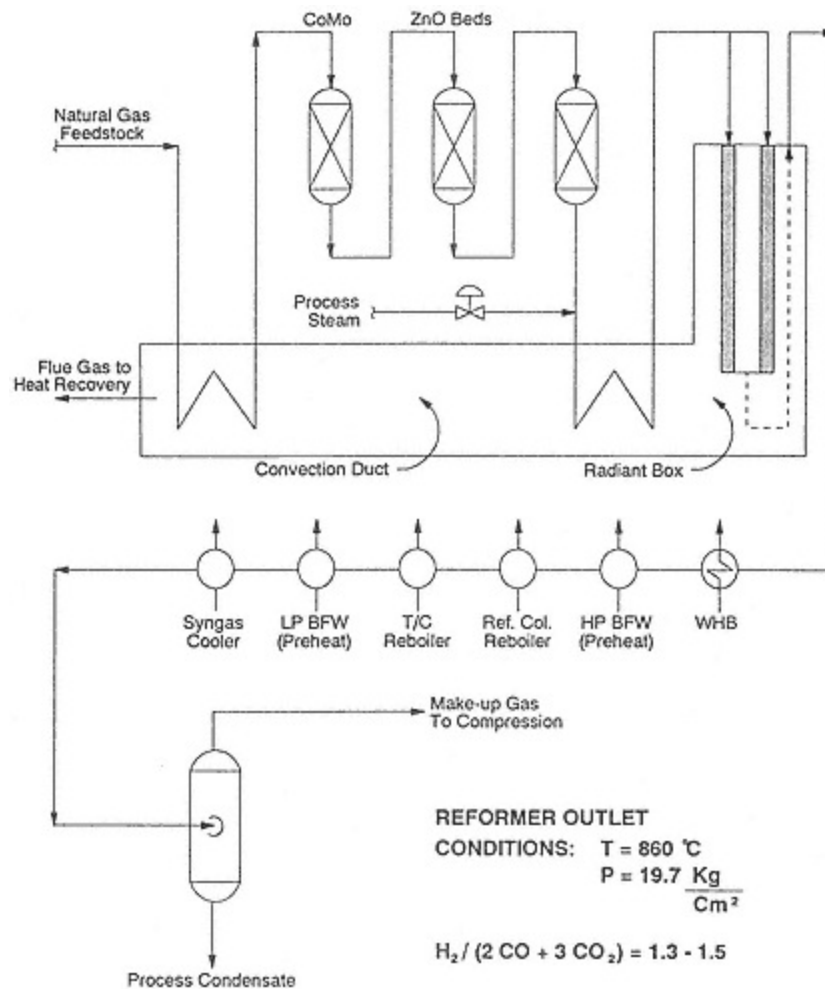


Figure 17  
Natural gas steam reformer.  
(Diagram courtesy of The M. W. Kellogg Company.)

A typical steam reforming schematic is given in Figure 17 [18]. Note the relative simplicity of this process. A light feed gas is simply preheated, desulfurized, mixed with steam, and then reformed and cooled before being compressed as feed to a methanol synthesis reaction loop. The process steps utilized in the steam reforming of a natural gas feedstock are described in somewhat more detail in Section 3.4.

Considering a plant designed to produce 2500 tpd methanol based on the aforementioned feed gas, the following feed and fuel requirements are estimated for a plant utilizing 10 MPa synthesis and steam reforming for syngas generation [18]:

Feed, Gcal/h, 755.99  
 Total reformer duty, Gcal/h, 350.29  
 Feed and net fuel, Gcal/h, 826.42  
 Specific gas consumption, Gcal/t, 7.934 (LHV basis)

This specific gas consumption figure is on an LHV (lower heating value) basis and is equivalent to approximately 31.5 MMBtu/t. This value is representative of the energy required not only to produce 2500 t/day of methanol plant but also to support all required off-sites, such as power generation, desalination of sea-water for boiler feedwater if required, and cooling water circulation. Battery limits energy consumption for a plant of this capacity would be about 2 MMBtu/ t less.

The thermal efficiency of the process as described (LHV of methanol/LHV of feed + fuel) is approximately 60%. This value lies within the expected range for the process. Implicit in these energy calculations is the assumption that excess H<sub>2</sub> produced by reforming (which is purged from the synloop), plus any letdown or distillation and light end vents, is burned as fuel in the reforming furnace.

Energy values quoted are deemed to be typical in nature. Specific feed and fuel consumption for any particular steam reforming-based plant depend upon exact gas composition, site climatic conditions, degree of available existing site infrastructure, and project economics.

### 3.3.3.1

#### The CO<sub>2</sub> Addition Alternative

When CO<sub>2</sub> is available nearby (as when a methanol facility is located adjacent to an ammonia plant), it makes a balanced syngas ( $R = 1.0$  approximately) possible by judicious addition to the process gas either upstream or downstream of the reformer. Typically, about 1 mol CO<sub>2</sub> may be added to every 4 mol natural gas feed to balance the syngas chemically so that it is nearly stoichiometric as it enters the methanol synloop. For new plants, CO<sub>2</sub> may be most often added as an auxiliary feed to the reformer, but when CO<sub>2</sub> is added to an already operating plant, addition is likely into the suction of the syngas compressor or directly into the synloop. Energy differences on an overall basis between these various alternatives are virtually nil. CO<sub>2</sub> provides additional methanol make (by balancing out the excess H<sub>2</sub> produced by steam-methane reforming) in an almost mole per mole ratio but also adds additional H<sub>2</sub>O to the crude, which must be removed in distillation. Higher CO<sub>2</sub> syngases are more stoichiometric but also

result in a loop carbon efficiency perhaps 12% less than that expected with a low carbon feed (where  $R = 1.31.4$ ).

CO<sub>2</sub> addition results in reduced loop purge gas, which in turn means that additional natural gas is required as fuel to the reformer. CO<sub>2</sub> addition is a proven process enhancement, and there are many industrial demonstrations of the concept.

### 3.3.4 Combined Reforming

The process of combined reforming (also variously known as combination reforming or oxygen-enhanced reforming) utilizes both a primary and a secondary (or autothermal) reformer in series for production of synthesis gas, as is commonly practiced in ammonia manufacturing. The secondary in the case of methanol, however, is injected with nearly pure oxygen (99.5+%) rather than air since the presence of excessive N<sub>2</sub> in the syngas would overburden compression and retard methanol synthesis. Figure 18 [18] displays one possible scheme for employing this process. By introducing oxygen into the secondary, excess H<sub>2</sub> is combusted, and a nearly stoichiometric ( $R = 1.0$ ) synthesis gas may be produced from a natural gas feedstock. Combustion in the upper zone of the secondary (or autothermal reformer) increases the temperature of the partially combusted gas (feed is primary reformer effluent), which then drops rapidly in the catalytic zone, where the endothermic reforming process "soaks up" heat as it proceeds axially along the reactor catalyst bed.

By shifting some of the reforming duty from the primary reformer to the secondary reformer, the primary size (in new plants) and fired duty are reduced. It is generally found advantageous in this process to reduce the primary reformer catalyst exit temperature (say from 860 to 730°C) while increasing the primary exit pressure from about 2 MPa (20 atm) to 3.8 MPa (38 atm). This save energy further by reducing syngas compression requirement while maintaining an acceptable catalyst tube life.

The key to success in this process is in the design of the secondary reformer, in particular the design of the burner apparatus in the combustion zone. Figure 19 gives one example of a commercially proven design (Kellogg unit) that has been successfully used in both H<sub>2</sub> and methanol service in which pure oxygen injection was employed. Ultimately, oxygen injection rates in this process must be limited by such considerations as the degree of mixing expected in the combustion zone and the expected reliability of the refractory and refractory support system within the lined reactor. The safest design for a secondary reformer injected with pure oxygen would employ not only the requisite refractory lining and recommended external water jacket but also a safe upper limit on the amount of oxygen added to the system.



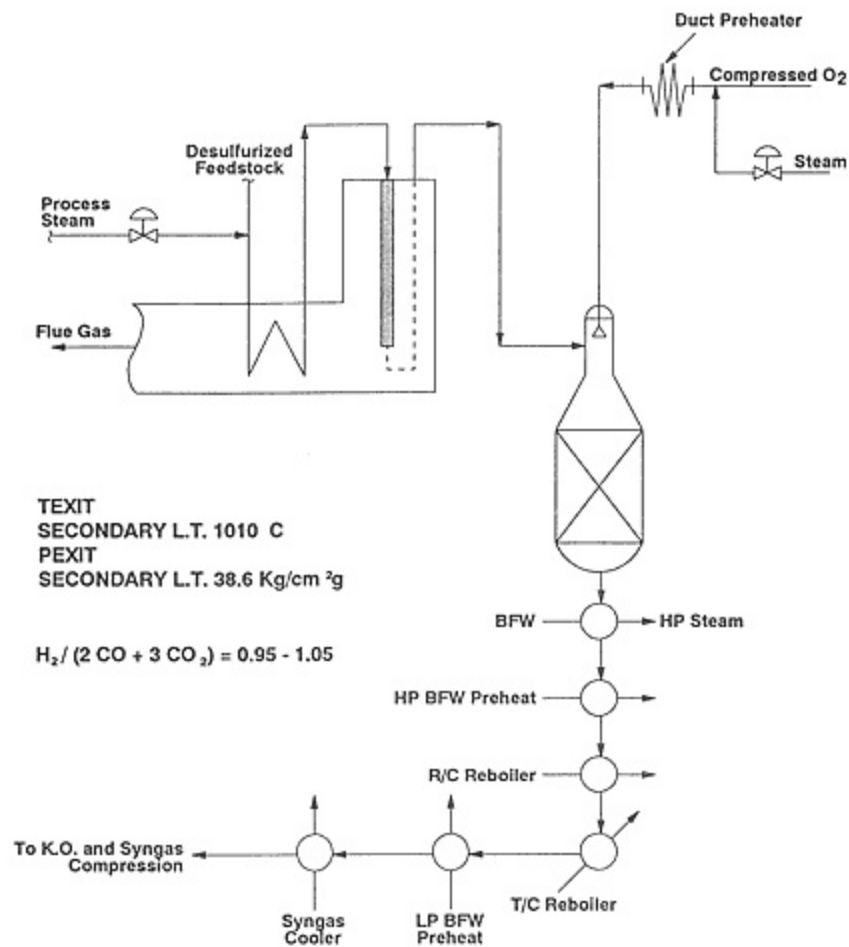


Figure 18  
Combined reforming diagram.  
(Courtesy of The M. W. Kellogg Company.)

Consider a case comparison whereby 2500 tpd of methanol was produced via combined reforming by adding 0.4 t O<sub>2</sub>/t MeOH to the secondary reformer (nearly 1000 tpd O<sub>2</sub> required). The feed gas was similar to that discussed in Section 3.3.3 describing the steam reforming of natural gas. Table 7 compares steam reforming and combined reforming for the same size of plant. In that comparison, a grass roots complex with all supporting utilities was the basis. Power was generated within the process (steam turbogenerator furnished) to operate the air separation facility, which required approximately 15,420 kW for air

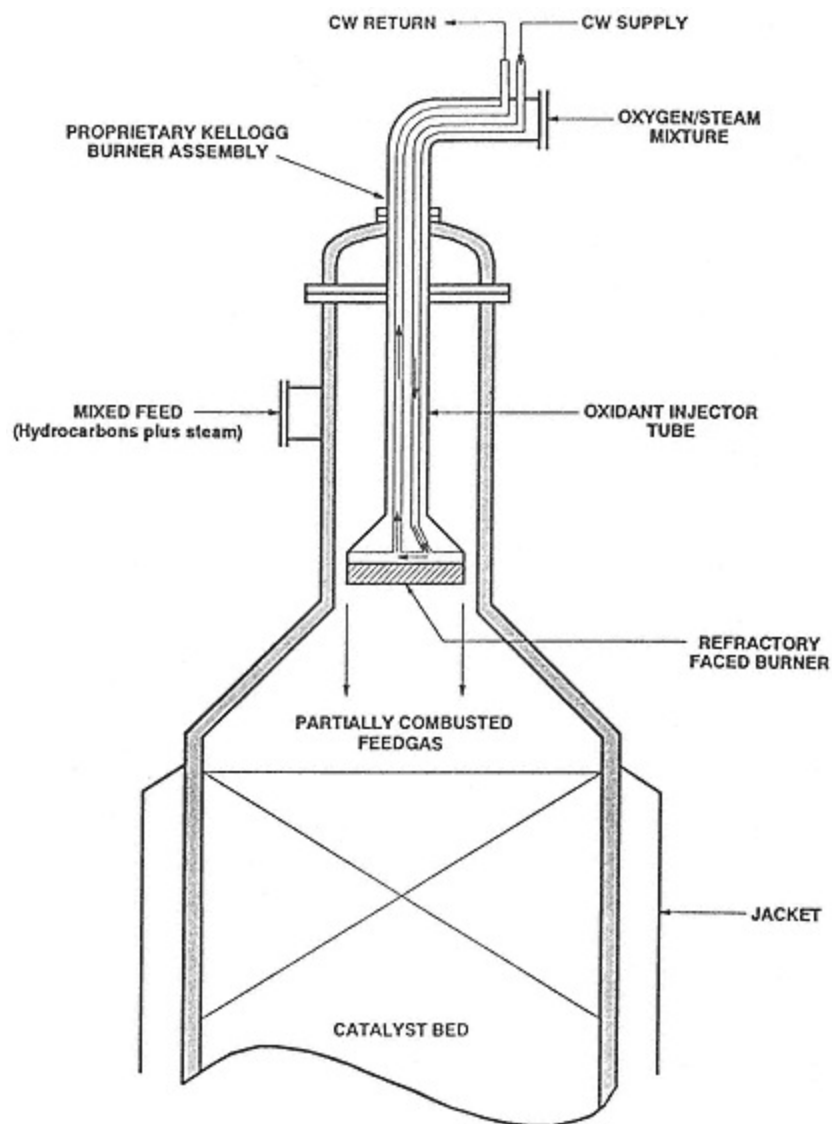


Figure 19  
Autothermal reformer with water-cooled burner.  
(Courtesy of The M. W. Kellogg Company.)

compression plus oxygen compression to process requirements. Table 7 shows that the combined reformer duty is reduced by about 45% (versus the base case of steam reforming) and makeup gas compression power is expected to drop by about 50%. Impressive savings to be sure: however, these are mostly offset by the high cost of air separation. On an overall basis, a savings of 2.2% favoring combined reforming was indicated (0.18 Gcal/t). Other cases may save somewhat more energy than indicated in the preceding example. Typically, the expected savings are in the range of 24% favoring combined reforming.

The M. W. Kellogg Company has successfully employed combined reforming for both H<sub>2</sub> and methanol production. Lurgi has built at least two commercial methanol units based on their combined reforming process. Details of the Lurgi process are given in References 19 and 20.

Different process licensors take a slightly different approach in the exact equipment and piping arrangement for combined reforming. The approach can have a major effect on the cost of the furnace, which represents a substantial portion of the inside battery limits capital investment. Accordingly, there is some variation in both energy savings and cost differentials predicted. In combined reforming, the furnace is substantially smaller and compression requirements are considerably reduced. However, the high cost of air separation and oxygen compression facilities has been found by several designers to more than offset the expected savings, resulting in a plant cost approximately 15% more than one of a similar capacity based on steam reforming of natural gas.

This increased capital requirement could only be justified with exceedingly high energy costs. There are significant environmental benefits to consider in combined reforming, however. Reduced firing reduces NO<sub>x</sub> (perhaps by as much as 70%) and CO<sub>2</sub> emissions. CO<sub>2</sub> is not reduced as dramatically as NO<sub>x</sub> in combined reforming since reduced H<sub>2</sub> in the loop purge means that additional firing with CH<sub>4</sub> is required in the primary reforming furnace.

Table 7 Comparison of Steam Reforming and Combined Reforming of Natural Gas

	Steam reforming of natural gas	Combined reforming of natural gas
Feed, Gcal/h	755.99	660.06
Utilities, Gcal/h	68.99	46.41
Total reformer duty, Gcal/h net	350.29	192.50
Feed and net fuel, Gcal/h	826.42	807.90
Specific gas consumption, Gcal/t	7.934	7.756

Combined reforming has been successfully applied in grass roots applications, but it may find its best application in the potential retrofit of ammonia plants to methanol manufacturing. Use of combined reforming in a retrofit enables the ammonia producer to convert to methanol production and maximize production while achieving an acceptable return on investment (pretax, internal rate of return, IRR, of more than 20%).

Conclusions regarding combined or oxygen-enhanced reforming can be briefly summarized as follows:

The process is proven; several commercial units have been built.

Reliability is a key issue; special attention should be paid to the design of the autothermal reformer, particularly the O<sub>2</sub>/feed gas mixer/burner.

O<sub>2</sub> injection rates should be limited to ensure that practical design limitations are not exceeded.

Gas consumption can, in some cases, be dramatically reduced, but on an overall specific energy consumption basis, 24% savings are probably achievable compared with a process based on steam-methane reforming.

NO<sub>x</sub> emissions may be reduced by roughly 70% without the use of selective catalytic reduction to treat the flue gas.

CO<sub>2</sub> emissions may be reduced by about 13%.

Plant cost is about 15% more than one based on steam-methane reforming.

Plant complexity for the process may result in on-stream factors less than those typically expected for the steam reforming process.

Gas costs of over \$5/MMBtu will likely be required to pay out the extra capital requirements of combined reforming; however, environmental benefits can potentially reduce the threshold gas cost for justification.

Combined reforming can be an attractive option for retrofitting an existing ammonia plant to methanol production.

### 3.3.5

#### Heat-Exchange Reforming

Heat-exchange reforming provides the plant operator with a process for producing methanol syngas without the use of a tubular fired reformer or a partial oxidation/coal gasification alternative front end. The concept is relatively simple. By linking a tubular heat-exchange reformer and an adiabatic or autothermal reformer, a simplistic reforming operation is arrived at whereby the heat generated in the autothermal unit is used to heat the process gas reacting within the heat-exchange reformer. Figure 20 gives one example of a Bayonet heat-exchange reformer. In a unit of this design, the heat-

exchange reformer and autothermal (or secondary) reformer operate in series. Hydrocarbon feed (generally a light natural gas) plus steam enters the heat-exchange reformer between

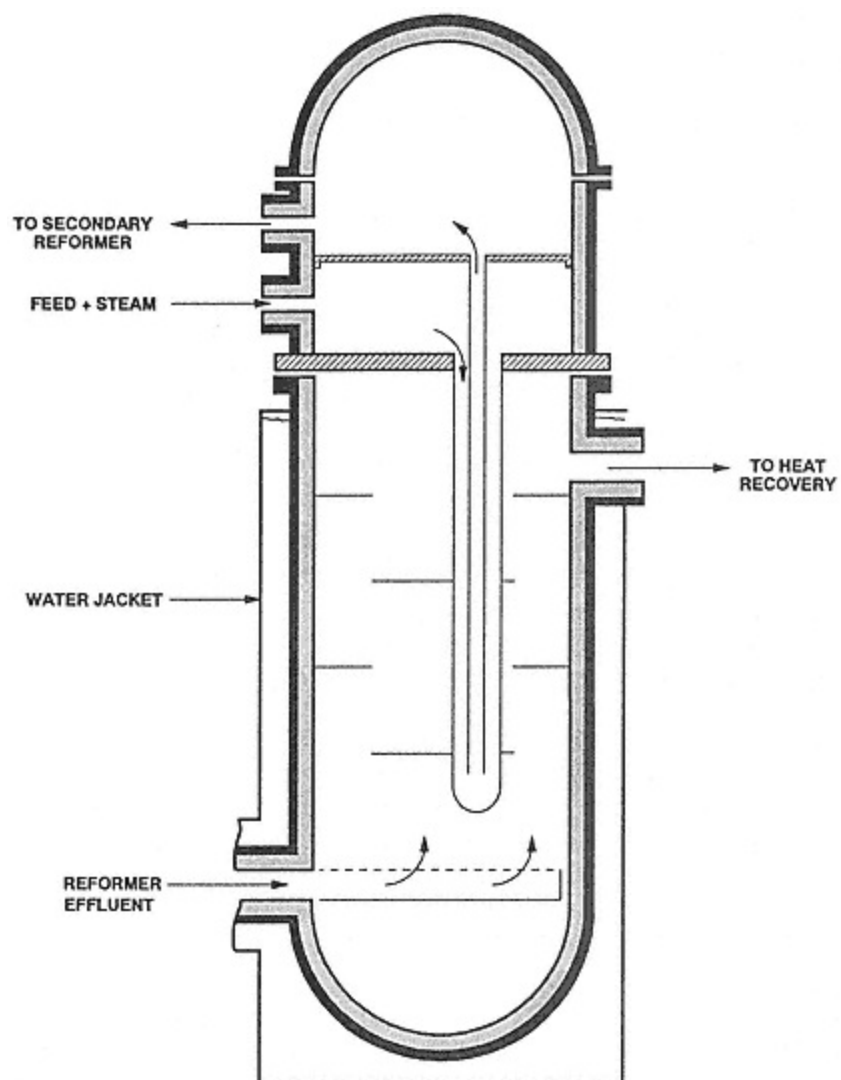


Figure 20  
Bayonet reforming exchanger.  
(Diagram courtesy of The M. W. Kellogg Company.)

two upper located tube sheets. The process gas passes axially downward through an annular space filled with conventional nickel-based steam reforming catalyst, where the reforming reaction takes place. The gas exits the catalyst at the bottom of the annular space and then passes upward through a center tube, where some sensible cooling takes place. The effluent exits above the top tube sheet, where it then passes to the secondary, where reforming is completed in the normal fashion. The gas exiting the bottom of the secondary reformer then passes to the bottom of the heat-exchange reformer shell, where it passes upward through the baffled section of bundle, providing the heat requirement for the heat-exchange reformer. The gas exiting the shell then passes onto a boiler or feed-effluent exchanger, where cooling takes place before the compression step. ICI has proposed a heat-exchange reformer similar to this design for methanol in their leading concept methanol process. They have commercialized the design (which they call a gas-heated reformer) in two small ammonia plants located in the United Kingdom.

Kellogg has proposed an alternative process, which is called KRES (Kellogg reforming exchanger system) and is schematically displayed in Figure 21. This process utilizes a patented open-tube reforming exchanger that is pictorially described in Figure 22.

In KRES, the secondary (or autothermal reformer) and reforming exchanger operate in parallel rather than in series. Process feed gas plus steam passes in parallel to the secondary and the reforming exchanger. In the secondary (as in combined reforming), pure oxygen is used for partial combustion of the hydrocarbon feed. The feed stream entering the reforming exchanger passes downward through a multiplicity of catalyst filled tubes, where significant reforming takes place. The secondary effluent and reforming exchanger catalyst tube effluent combine in the bottom shell of the reforming exchanger before passing upward through the shell as heat is provided to the catalyst-filled tubes by sensible cooling of the mixed gas stream.

Reforming pressure for the heat-exchange process is optimally in the 3.54.2 MPa (3542 atm) range. Pure oxygen requirements are about 0.5 ton oxygen per ton refined methanol product. The key theoretical reactions involved in the heat-exchange reform process (which equally apply to combined reforming) are as follows:



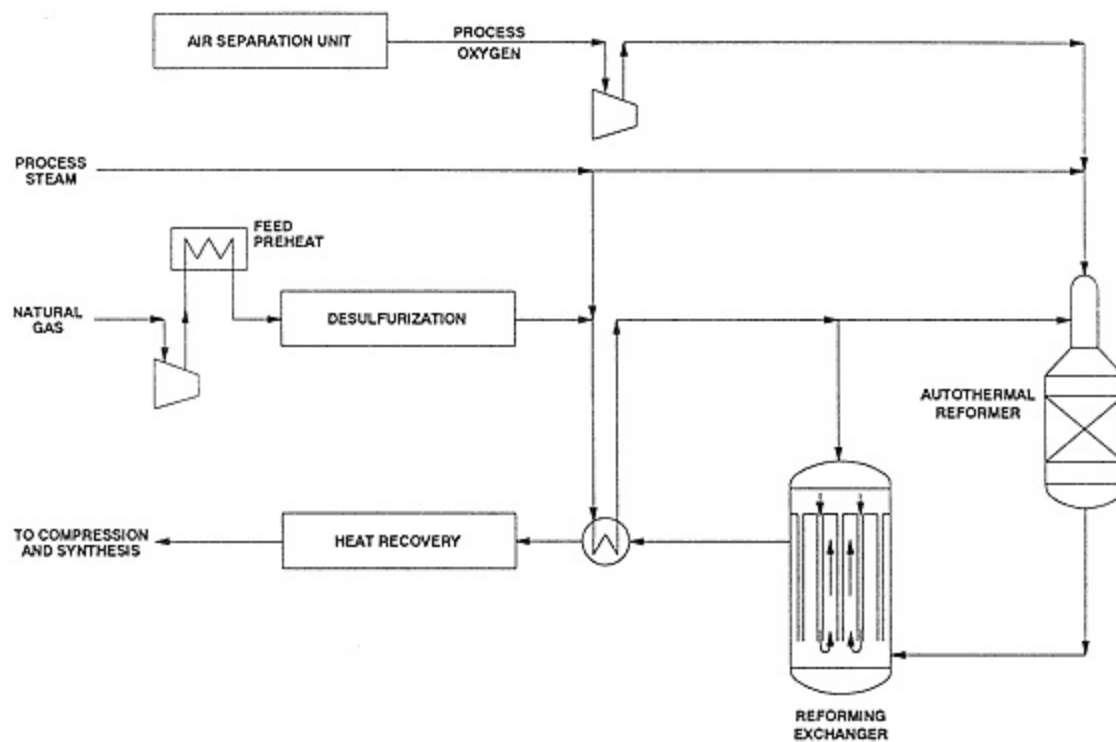


Figure 21  
Simplified diagram of the Kellogg reforming exchanger system (KRES).  
(Courtesy of The M. W. Kellogg Company.)



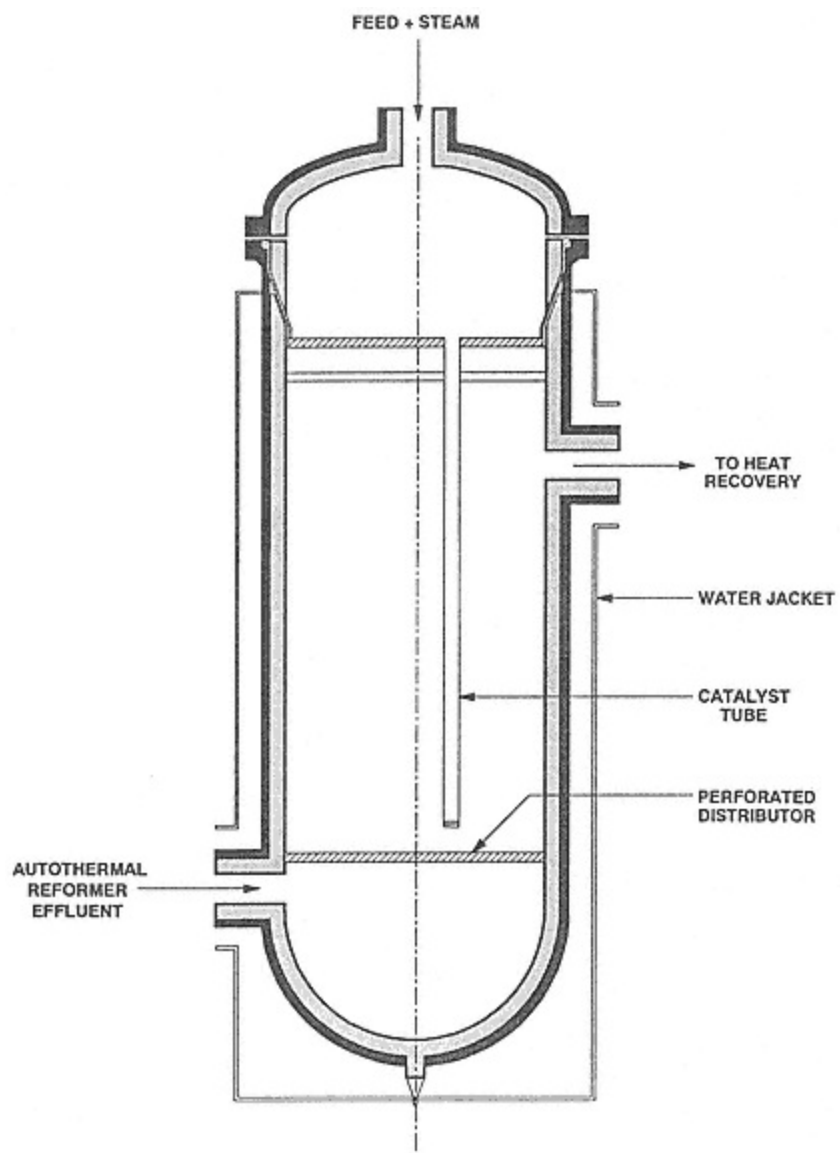


Figure 22  
Kellogg open-tube reforming exchanger.  
(Courtesy of The M. W. Kellogg Company.)



Note that a nearly stoichiometric feed is possible in this case, as with combined reforming.

The lack of fired reformer provides an ideal opportunity for integrating a gas turbine into the process. Utility duties can be handled in the turbine exhaust duct, and an overall improvement in energy utilization is made possible since the gas turbine with associated heat recovery can achieve a thermal efficiency of over 85%; the steam cycle normally exploited in a fired reformer application (where waste heat generates steam that drives the syngas compressor turbine) is generally limited to about 33%.

The advantages of the heat-exchange reforming processes include the following:

Operational flexibility is increased.

They are as or more reliable than a conventional plant.

Maintenance costs are reduced.

Overall complex energy savings of about 0.4 Gcal/t are expected.

Units are compact and require less space.

As in combined reforming, emissions of NO<sub>x</sub> and CO<sub>2</sub> are significantly reduced.

Commercialization of the Kellogg KRES design is set for an ammonia plant expansion in Canada that will start up in 1994.

### 3.3.6

#### Relative Comparison of Syngas Preparation Processes

Design of the methanol synthesis loop and accompanying distillation train is generally based on the following considerations:

Design preferences

Expected reliability and operability

Capital cost considerations

Generally speaking, the energy consumption differences between the various loop designs (based on quench, adiabatic-intercooled, and isothermal reactor systems) are very small and therefore not sufficiently large to make a choice on this basis alone. The choice of a syngas preparation process is much more difficult, however. This choice must consider a number of factors, including the following (but not limited to them):

Feedstock availability

Feedstock composition

- Cost of feed and/or fuel
- Plant location
- Complexity of integration with existing facilities (if any)
- Required reliability
- Environmental constraints
- Capital cost considerations

Of course, it should be obvious that there is no single "best" choice for syngas preparation. Every site has its own particulars, which demand consideration, and every project has specific goals that must be met. These circumstances affect what is considered the optimum choice in any given instance.

However, the following apply generally. Steam reforming of natural gas will undoubtedly continue as the process of choice for most new methanol installations. Energy efficiency for this route is competitive; the reliability is such that on-stream factors of well over 90% are possible, and the capital cost will generally be the most attractive of all potential alternatives. Single-train capabilities of up to 3000 tpd are possible with this proven technology.

Coal gasification and partial oxidation alternatives appear to be niche applications that fit only in select and special cases. These processes are more complex and less reliable than steam reforming and are higher in capital cost. Nonetheless, future special-purpose applications may favor these technologies, such as in combined cycle power generation. In this case, a coal gas feed linked to a liquid-phase synloop may be an attractive design alternative.

Combined reforming and heat-exchange reforming both are somewhat more efficient than steam reforming. At this point, use of a reforming exchanger-based system appears to offer the lowest energy consumption with the minimum amount of equipment required. Both processes are expected to cost more than a steam reforming-based plant. Other benefits may swing the decision in favor of one of these options, however, even at lower gas costs.

Combined reforming seems particularly attractive for maximizing production when retrofitting an existing ammonia plant for methanol production.

### 3.4

#### Steam Reforming of Natural Gas to Methanol

Natural gas is the most common raw material used in the manufacture of methanol. More than 75% of all the methanol produced worldwide is produced from natural gas. The flow scheme for a typical large-capacity methanol plant is depicted in Figure 23. The processing steps include feed gas pretreatment, steam reforming, waste heat recovery, synthesis gas compression, methanol synthesis, and distillation.



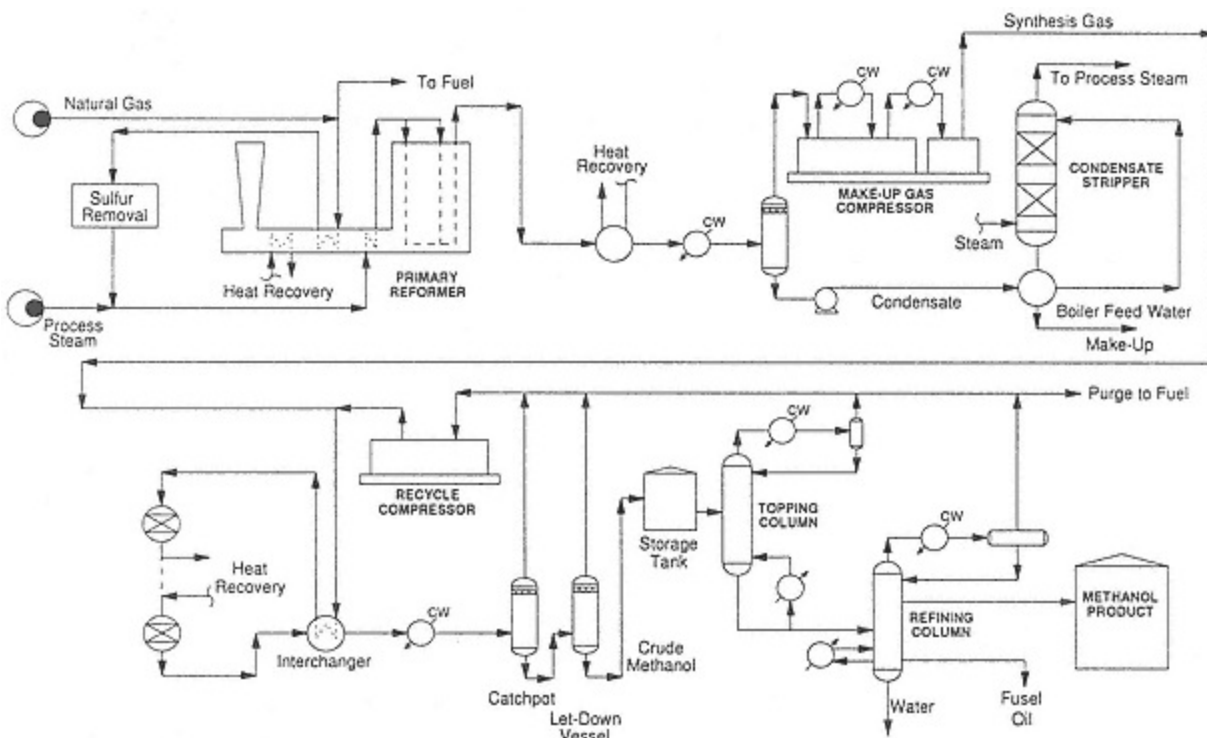


Figure 23  
Simplified methanol flow diagram.

### 3.4.1

#### Pretreatment

The natural gas feedstock must be clean and dry. The sulfur compounds normally found in pipeline natural gas must be removed to prevent poisoning and subsequent deactivation of the reforming and methanol synthesis catalysts. Starting with pipeline natural gas typically containing no more than 50 ppmv sulfur, the natural gas stream is heated to 260°C. A small amount of hydrogen recycle is added so that the organic sulfur compounds are hydrogenated to H<sub>2</sub>S across a CoMo or NiMo catalyst, and subsequently the H<sub>2</sub>S is absorbed on a bed of ZnO catalyst. In this manner the sulfur content of the feedstock is typically reduced to less than 0.1 ppmv. Zinc oxide beds used in this type of application are typically sized for a minimum bed life of 6 months to 1 year. The most common arrangement is to allow two ZnO beds to operate in series, with actual bed change based on an observation of interbed sulfur breakthrough.

Higher hydrocarbons present in natural gas can be beneficial to the production of methanol but detrimental to the operation of the reformer. Hydrocarbons higher than methane contain a higher ratio of carbon to hydrogen and generate a more stoichiometric synthesis gas. For a given heat content a heavier gas produces more methanol than a gas containing methane only. The fired reformer performance can be adversely affected by higher hydrocarbons, however, resulting in uneven heat flux in the catalyst-filled reformer tubes and the potential for hot bands and carbon formation in the tubes.

An adiabatic reformer (prereformer) upstream of the fired reformer permits the use of heavier feedstocks while reducing the load on the reformer for higher throughput and improved efficiency [21]. After desulfurization, the feedstock and steam are heated to 500-550°C and passed through a bed of special nickel/alumina prereforming catalyst. The reactions occur adiabatically, and all higher hydrocarbons are converted to methane; a portion of the methane is reformed to hydrogen and carbon monoxide. The process gas cools as the reactions take place, and the prereformer effluent is then reheated before entering the reformer tubes. A prereformer provides a portion of the reforming load, and therefore a smaller reformer can be used. Also, fuel need not be burned to heat the prereformer feed since the temperatures are low enough that process or flue gas heat can be used. This permits a more efficient design and less generation of nitrous oxides. Figure 24 displays a schematic for a typical prereformer installation.

Prereforming is not a widely used practice, due in part to the limited number of commercially available catalysts and more specifically to the wide use of light natural gas feedstocks for methanol manufacture. In recent years more active and stronger prereforming catalysts have been successfully demonstrated in commercial operation, and these will likely be used more frequently when heavy

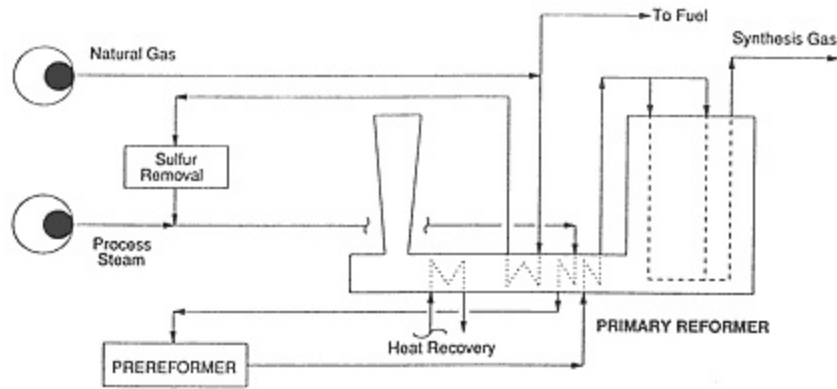
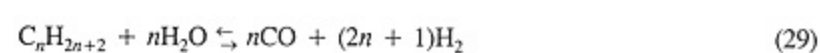


Figure 24  
Prereformer flow diagram.  
(Courtesy of The M. W. Kellogg Company.)

feedstocks, such as LPG and naphtha, are used as a methanol plant feedstock. With prereforming, the plant operator may operate a fired reformer at more or less normal steam-carbon ratios while using conventional nonpromoted catalysts and higher hydrocarbon feeds.

### 3.4.2 Steam Reforming

Following feed pretreatment, the next step in the preparation of methanol synthesis gas is the steam reforming of the natural gas to form a mix of hydrogen and carbon oxides. Two principal reactions take place in the steam reformer: reforming [Eq. (29)] and water-gas shift [Eq. (20)]. The predominant reaction taking place is the steam reforming of methane [Eq. (21)].



The overall reaction within the reformer is endothermic, and conversion is enhanced by high temperature, low pressure, and high steam-carbon ratios.

The steam reformer is a large process furnace in which catalyst-filled tubes are heated externally by direct firing to provide the necessary heat for the reactions taking place inside the reformer tubes. In methanol service, fired tubular reformers typically come in two principal types: downfired and side-fired.

In the downfired design the burners are located at the top of the furnace alongside the top of the reformer tubes. The feed gas and hot flue gas flow in parallel down the length of the tube. The tubes are manifolded together to collect the synthesis gas, which passes back up through the furnace in riser pipes that collect more heat before passing into the effluent transfer line and out of

the reformer. Some top-fired designs allow a bottom exit where gas exits the catalyst filled tubes through pigtails before passing to external collection manifolds. The flue gas is pulled out of the radiant section of the reformer through the convection section, where additional heat is extracted to increase overall furnace efficiency before final discharge to the atmosphere.

Contractors offering downfired furnaces for methanol applications include ICI licensees, such as Davy Technology (division of John Brown) and Humphreys and Glasgow, Uhde, KTI, and The M. W. Kellogg Company. (See Figs. 25 and 26.)

Side-fired furnaces have many small burners located at each side of the radiant box, firing directly at a centrally located single row of tubes. For large plants, typically two or more cells are required. Selas and Topsøe offer furnaces of this design.

The Foster Wheeler reformer furnace is a Terrace-Wall furnace. The unique feature of this side-fired design is the burner location (Fig. 27 and 28). The burners are directed at the walls of the furnace, which radiate heat to the tubes. As with the top-fired reformer, the process gas enters the top and passes to the bottom. Unlike many top-fired furnaces, the terrace-walled furnace tubes have

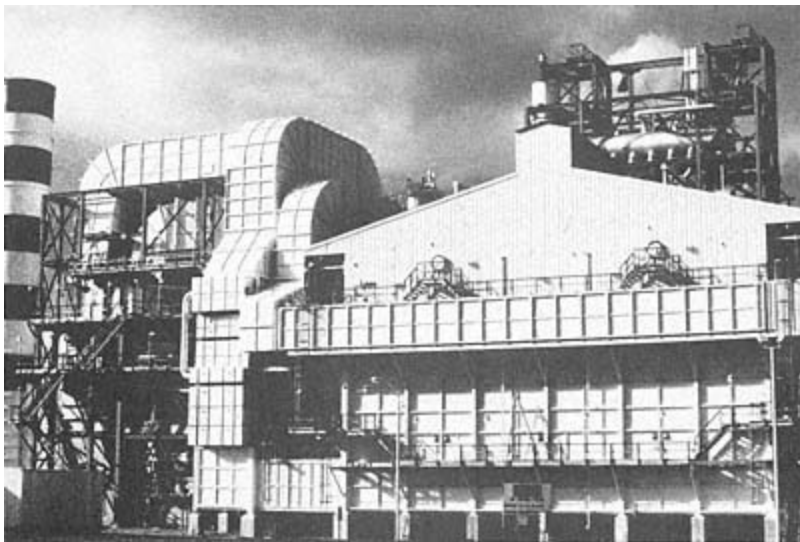


Figure 25  
Steam reformer at Cape Horn Methanol plant near Cabo Negro, Chile.  
(Photograph courtesy of The M. W. Kellogg Company.)



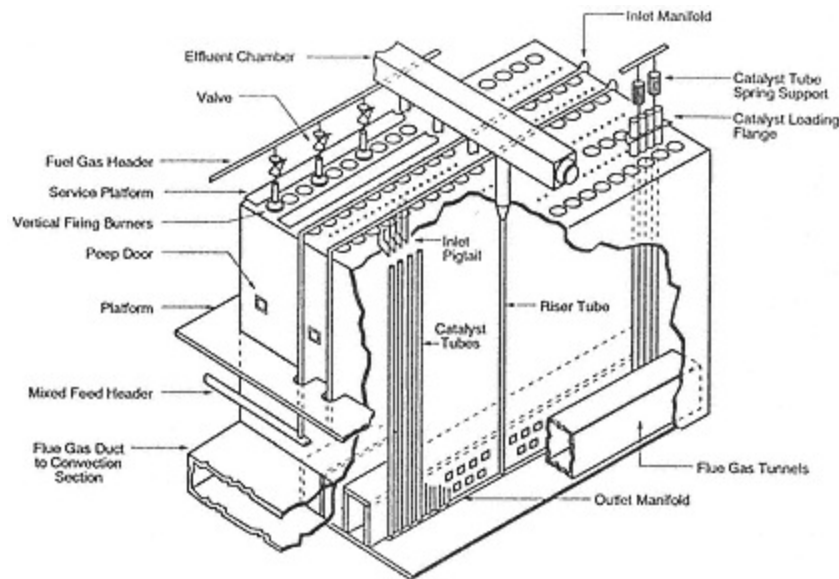


Figure 26  
Kellogg downfired steam reformer.  
(Courtesy of The M. W. Kellogg Company.)

an exit at the bottom of the reformer. The flue gases pass up and out the top of the reformer. Burners are located along the walls of the furnace principally at two distinct locations, the upper and lower terraces. Functionally the two types of furnaces are the same. They provide the heat required for the process reactions and recover heat from the flue gas to increase the efficiency of the furnace.

Until the 1980s most reformer furnaces were constructed using centrifugally cast 25% chromium and 20% nickel (HK-40) alloy tubes. More recently, however, a higher strength 25% chromium and 35% nickel-niobium (HP modified) cast tube is being used. The newer tube material is stronger (as evidenced by greatly improved stress-to-rupture properties) and can result in thinner tubes containing less net metal for the same design tube life.

The radiant box of the reformer is typically about 50% efficient. Thus, to ensure a thermodynamically efficient operation, the heat liberated but not absorbed in the reforming reaction must be recovered in the convection section of the reforming furnace. Typically the reformer flue gases are reduced to about 150°C, resulting in an overall furnace efficiency of 92-93%.

Hot flue gases are typically used to heat mixed streams of steam and natural gas feed to the reformer, steam only, fuel gas, boiler feedwater, and combustion air.

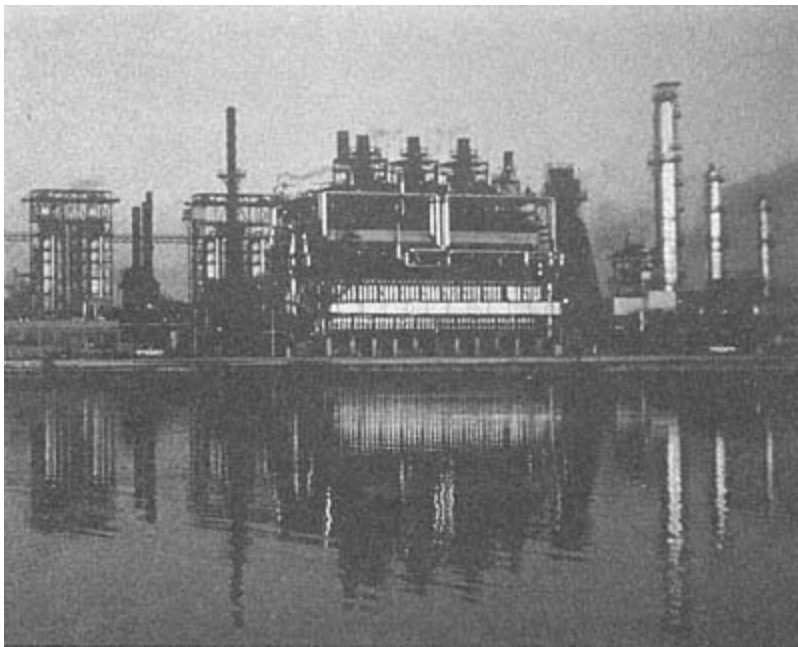


Figure 27  
Foster Wheeler steam reformer.  
(Photograph courtesy of Foster Wheeler Corporation.)

### 3.4.3 Waste Heat Recovery

The methanol synthesis gas exiting the reformer is much hotter than required for the methanol synthesis reaction. To increase the efficiency of the process this waste heat is recovered back into the process just as the heat in the reformer flue gas is recovered to increase furnace efficiency. The process gas leaves the reformer typically at about 860880°C and first enters a steam boiler for the recovery of excess process heat. The steam raised in the boiler (after it has been superheated) is then used to provide motive power for compressor turbines and/ or process steam to the reformer.

There are two principal types of boilers for this steam generation downstream of the reformer: fired-tube boilers and water-tube boilers. In fired-tube boilers the hot process gas passes through the tubes of the boiler, steam being generated on the shellside. This Tubular Exchange Manufacturers Association BEM exchanger uses a fixed tube sheet design that does not permit the shell and tubes to grow thermally independent of each other. As a result this exchanger is constructed with a thick tube sheet and shell and high-strength connections between

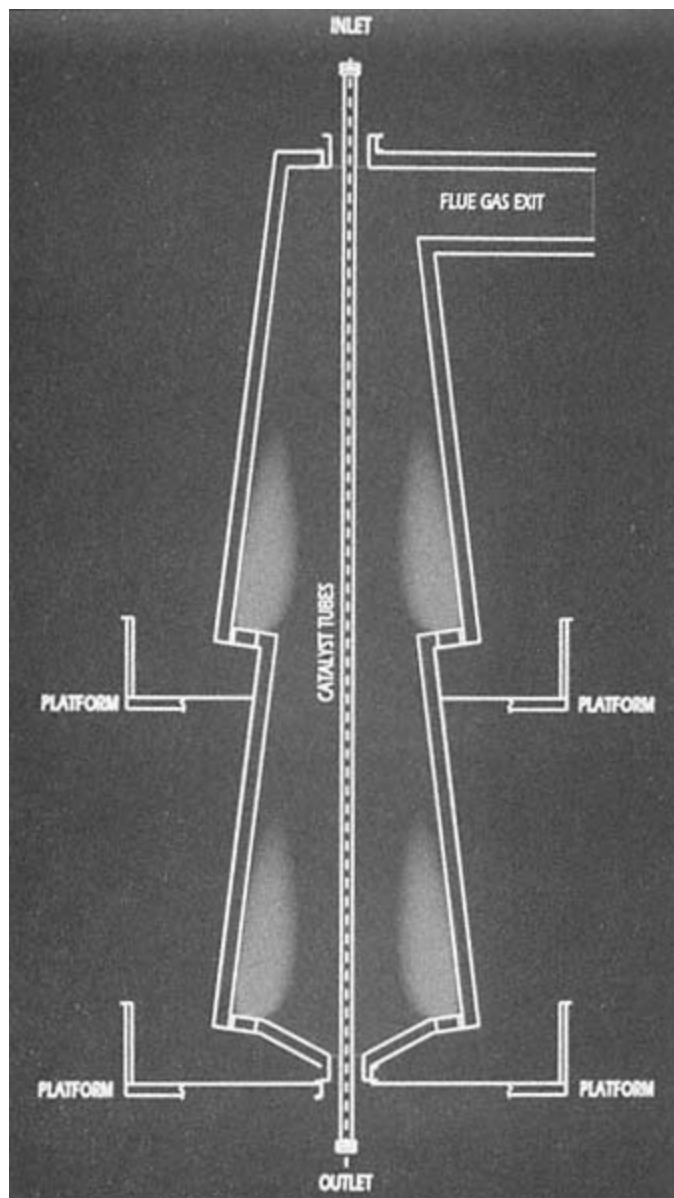


Figure 28  
Terraced®-wall steam reformer.  
(Courtesy of Foster Wheeler Corporation.)

the tubes and tube sheet. An alternative design for a fired-tube boiler is provided by Borsig (Fig. 29 and 30). The Borsig boiler uses a thin but strengthened tube sheet to reduce the impact of differential thermal growth on stress encountered in the tube-tube sheet joints. These types of boilers have found wide application in commercial methanol facilities.

Water-tube boilers, as the name implies, have water inside the heat-exchanger tubes, where steam is generated; the hot process gases are on the shell side. Water-tube boilers are partial vaporization boilers requiring some form of water circulation through the tubes to keep the tubes from becoming dry. This circulation is accomplished by pumping or natural circulation through an elevated steam drum. One such water-tube boiler is a floating-head heat exchanger as used by Kellogg (Fig. 31). With this design the differential thermal growth between the shell and tubes is taken up by the expansion joint, and the bundle can be removed from the shell for repair or replacement.

The high-temperature process heat is normally recovered through steam generation; however, to make the overall process efficient, lower temperature process heat must also be used. Therefore, processes normally pick up the heat after the high-pressure boiler and use it to reboil the distillation columns in the purification section, raise low-pressure steam, and heat boiler feedwater or

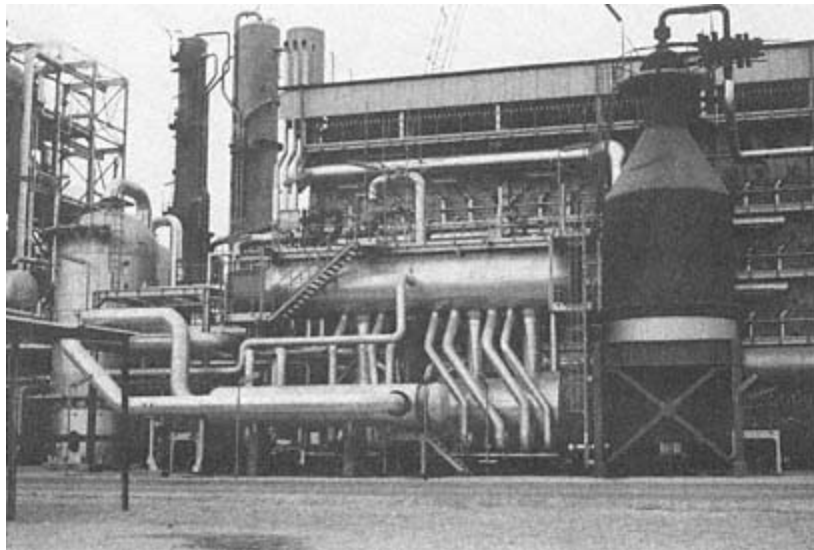


Figure 29  
Borsig fired-tube boiler.  
(Photograph courtesy of Babcock Borsig.)

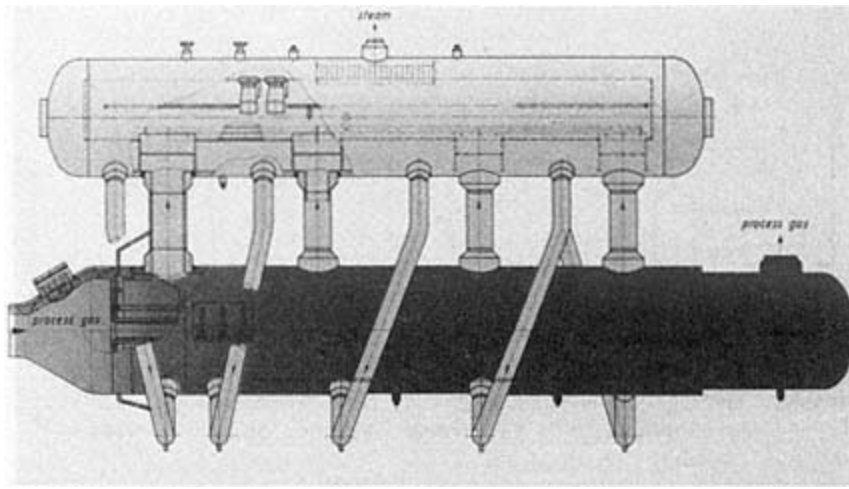


Figure 30  
Borsig boiler showing strengthened tube sheet.  
(Courtesy of Babcock Borsig.)

demineralized feedwater to the deaerator. Final cooling before compression is generally by heat rejection to cooling water.

### 3.4.4 Compression

At this point the synthesis gas is low in poisons, such as sulfur, and of the correct composition to react to methanol over the synthesis catalyst in the synthesis loop. Commercial methanol synthesis loops operate at 510 MPa (50100 atm) and the reforming takes place at 1.52 MPa (1520 atm) for typical steam reforming. Therefore the synthesis gas must be compressed (makeup gas compression) before conversion to methanol. The methanol synthesis reaction is a gas-phase equilibrium reaction, with about 48% conversion of the reactants to methanol achieved per pass across the catalyst bed or beds. Therefore it is necessary to condense crude methanol from the reactor effluent and then compress and recycle the unreacted reactants back through the reactor(s). In all large methanol plants this compression is accomplished with centrifugal compressors. Some processes combine the recycle compression and makeup gas compression in the same compressor. Other processes have separate makeup and recycle compressors. The combined makeup and recycle compressor has the advantages of a single compressor, but at the same time the speed of the recycle compressor section must be the same as the makeup compressor section. Having a single compressor train gives this concept a cost advantage. On the other hand, effi-

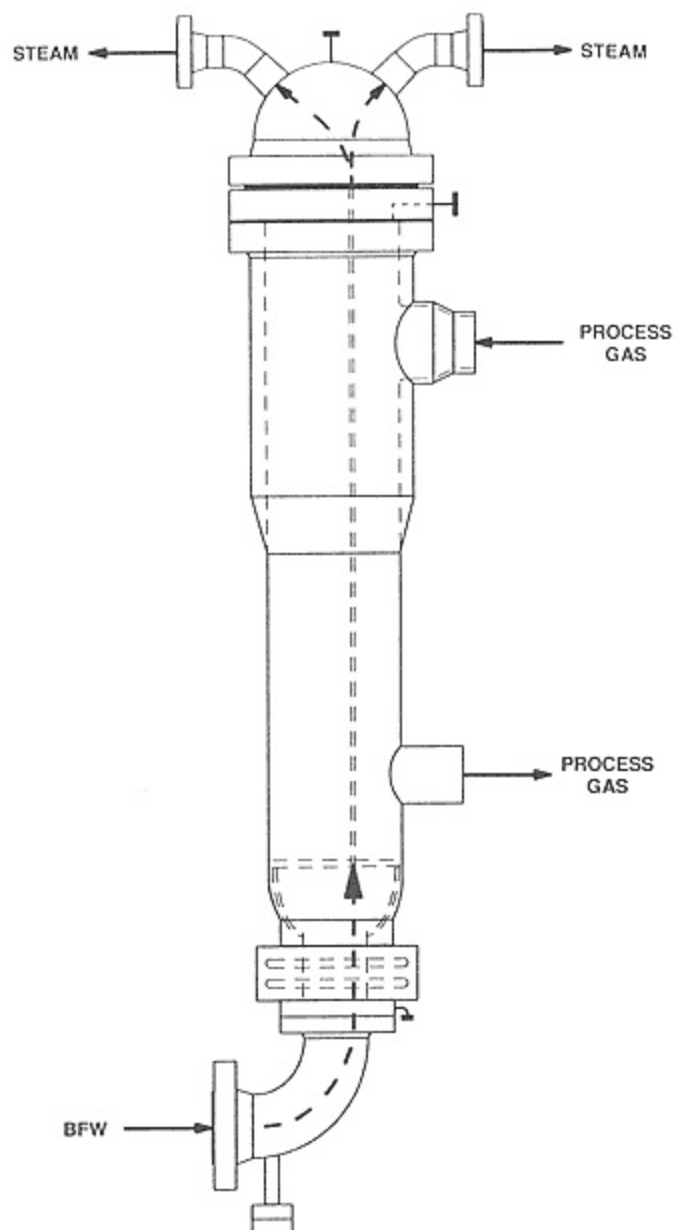


Figure 31  
Floating-head water-tube boiler.  
(Courtesy of The M. W. Kellogg Company.)

ciency is lost when the compressor operates away from its design point, and as methanol synthesis catalyst ages, varying amounts of recycle are needed for peak efficiency.

By separating the recycle compressor from the makeup compressor, the amount of recycle can be varied independently of the makeup compression required. Makeup gas compression is most dependent upon production rate. Recycle is most dependent upon methanol synthesis catalyst activity. As the catalyst deactivates, more and more recirculation is required. With a separate recycle compressor the recycle compression step operates efficiently over the full range of flow. When the recycle compressor is connected to the makeup compressor, the combined unit must operate inefficiently part of the time. It is somewhat more costly to have two separate compressors, but for efficiency reasons a separate recirculation compressor is normally chosen. Having a separate recycle compressor can also be beneficial for synthesis catalyst reduction purposes.

### 3.4.5 Methanol Synthesis

Central to the manufacture of methanol is the methanol synthesis catalyst. This Cu-Zn catalyst is poisoned by even small amounts of sulfur or chlorine compounds. Also, the catalyst is permanently deactivated by certain abnormal operating conditions, such as high temperatures and abnormally low  $\text{CO}_2/\text{CO}$  ratios. Considerable attention is given to controlling the conditions around the catalyst to maintain a highly active and selective catalyst.

The methanol conversion reactions are exothermic, and the heat of reaction is removed in each process to increase the conversion per pass through the reactor system. There are three basic types of gas-phase reactor systems: quench, isothermal, and intercooled.

ICI introduced the low-pressure methanol process with a quench reactor system. The ICI process is the most widely used, and therefore there are many quench reactors in methanol service. Other reactor systems have been developed over the years to improve upon the thermodynamics of the system, including pseudoisothermal reactors as used by Lürigi and Linde and intercooled reactors as used by Topsøe and Kellogg. These reactors are described in Section 3.2.5.

After passing across the catalyst to reach the maximum methanol concentration, the crude methanol, including water and reaction by-product impurities, is condensed from the synthesis gas. This crude methanol is sent to the purification section of the plant for further processing into product methanol; the noncondensables, including the reactant hydrogen, carbon monoxide, and carbon dioxide, are recycled and recompressed to pass across the synthesis catalyst again.



In plants with nonstoichiometric feedstocks, which is the case for most plants, hydrogen and methane build up in the synthesis loop and must be purged. The purge gas is generally used as fuel in the fired reformer.

3.4.6  
Distillation and Methanol Purification

U.S. federal grade specification O-M-232e identifies three grades of methanol. Grade C is for wood alcohol used in denaturing. Grade A covers methanol generally used as a solvent. Federal grade AA is the purest product and is used for chemical applications in which high purity and low ethanol content are required, such as for methyl tert-butyl ether manufacture [22]. The general standard observed by the industry for methanol product purity is U.S. federal grade AA (Table 8).

Crude methanol as removed from the synthesis section contains water and impurities, which must be removed before the product is ready for commercial use. Although fuel-grade methanol can be produced with a single distillation tower, two, three, and sometimes even four tower distillation systems are used to produce federal grade AA methanol. The amount of distillation required is dependent upon the by-product formation of the methanol synthesis catalyst, which includes esters, ethers, ketones, aldehydes, higher alcohols, and parafinic hydrocarbons. The amount of by-product is dependent upon the type and age of the synthesis catalyst and the operating conditions in the loop. The most problematic impurity is ethanol.

Table 8 Specification of U.S. Federal Grade AA Methanol

Component	Grade AA
Ethanol, mg/kg	< 10
Acetone, mg/kg	< 20
Total acetone and aldehyde, mg/kg	< 30
Acid (as acetic acid), mg/kg	< 30
Color index (APHA) <sup>a</sup>	< 5
Sulfuric acid test (APHA)	< 30
Boiling point range, I °C	< 1
Dry residue, mg/L	< 10
Density (20°C), g/cm <sup>3</sup>	0.7928
Permanganate number, min	> 30
Methanol content, wt%	> 99.85
Water content, wt%	< 0.10

<sup>a</sup> American Public Health Association.



The first column of any multicolumn system is the topping column, which operates at about 60 kPa (0.6 atm) to remove light ends (ethers, ketones, and aldehydes) and any dissolved gases remaining in the crude methanol, including hydrogen, methane, carbon oxides, and nitrogen. The topping column bottoms (sometimes referred to as "topped" crude) are further purified in one, two, or three refining columns.

The two-column system (Fig. 32) uses a single atmospheric refining column to separate the methanol from water and the higher alcohols (often referred to as fusel oil). Final separation is difficult and requires a large number of distillation stages. Particularly difficult is the ethanol-methanol separation, and one of the more common problems with off-specification methanol is ethanol in excess of 10 ppm. The product methanol is withdrawn a few trays down from the top of the refining column. The top of the column is used to reflux the column and separate any light ends that may have passed the topping column. The higher boiling alcohols move farther down the column and are extracted a few trays from the bottom. This methanol stream containing the heavier hydrocarbons, such as paraffins and higher alcohols, is commonly called fusel oil. The fusel oil has traditionally been burned in the primary reformer or utility boiler or further processed to separate the methanol from the by-products. Water is re-

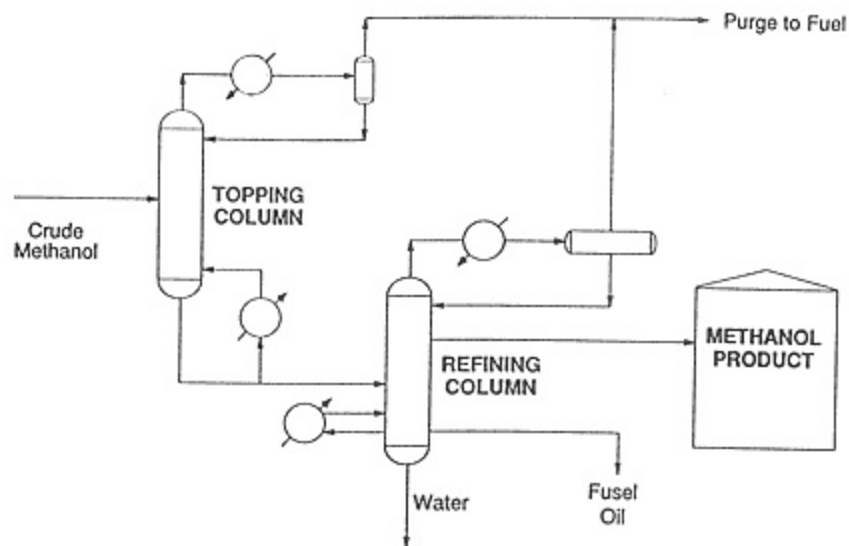


Figure 32  
Two-column methanol distillation.  
(Courtesy of The M. W. Kellogg Company.)

moved from the bottom of the refining column. This water is generally sent to some form of biological treatment to remove any organics.

In the three-column system (Fig. 33) the topping column bottoms passes first to a pressurized refining column and then to an atmospheric refining column. Federal grade AA methanol is withdrawn close to the top of both refining columns. Although the three-column system is more costly, it can reduce the required distillation heat input by 30-40% [23].

Occasionally a four-column distillation system is used, but most modern processes use either a two- or three-column system to produce U.S. federal grade AA methanol. Multicolumn systems (three or more columns; Fig. 33) can generally only be justified when the cost of energy is prohibitively high.

### 3.4.7

#### Energy and Utility Systems

A methanol plant is very energy intensive. The theoretical energy required to convert pure methane to methanol and hydrogen, Equation (27), is 5.97 Gcal (LHV)/t, and the theoretical energy required to produce methanol from ethane, Equation (30), is 5.32 Gcal (LHV)/t:

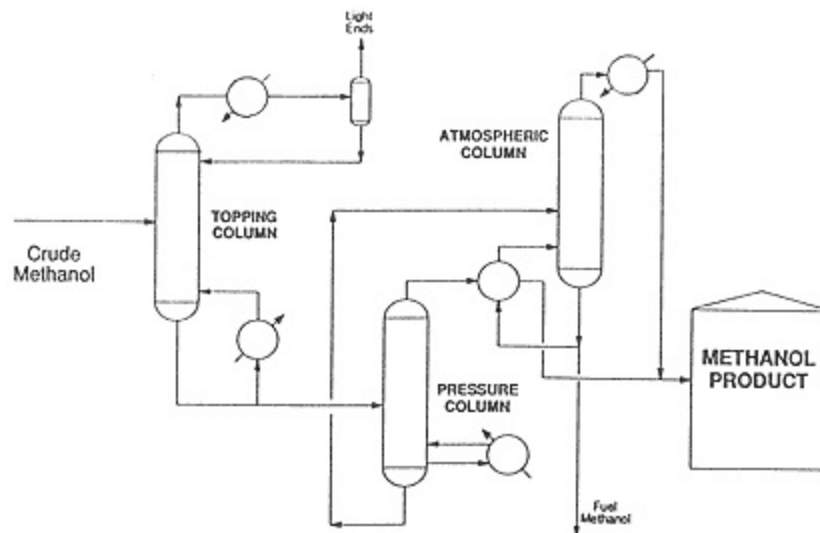


Figure 33  
Three-column methanol distillation.  
(Courtesy of The M. W. Kellogg Company.)

As the carbon content of the feedstock increases, the theoretical energy required to produce methanol decreases. This is why heavier feedstocks are often used for methanol production.

Because carbon is the limiting factor, the carbon conversion to methanol, also referred to as carbon efficiency, is an important operating parameter for overall energy efficiency. Carbon efficiency is a measure of how much carbon in the feed is converted to methanol product. There are two commonly used carbon efficiencies, one for the overall plant and one for the methanol synthesis loop. For the overall plant all the carbon-containing components in the process feedstock from the battery limits and the methanol product from the refining column are considered. For a typical plant and natural gas feedstock, an overall carbon efficiency is about 75%. The methanol synthesis loop carbon efficiency for the same plant is about 93%. The synthesis loop carbon efficiency is calculated using only the carbon in the reactive components in the makeup gas ( $\text{CO}$  and  $\text{CO}_2$ ). Carbon in the form of methane is not considered because it is inert in the methanol synthesis reaction and is ultimately purged from the loop and burned. The carbon in the product for this calculation is that in the form of methanol in the crude leaving the methanol synthesis loop.

The means by which the unreacted synthesis gas and by-products are used in the process have a significant impact on overall energy consumption. Hydrogen is purged from the synthesis loop, combined with the light ends from the topping columns and the refining column, and burned in the reformer. In other words, all the process gas purge streams are burned in the reformer, making use of these streams as fuel. The higher boiling by-products are contained in the fusel oil, which in most operations are also burned in the reformer. By burning almost everything but the product methanol in the high thermal efficiency reformer, none of the process feedstock is wasted. In many instances the purge from the process provides about 90% of the total fuel burned in the reformer.

Natural gas-based methanol plants typically consume 7.27.8 Gcal (LHV)/ t, depending on project specifics. How the fuel and process heat are used has a significant impact on the overall process energy consumption.

Heat is needed in the distillation steps, and steam is required for reforming and shift reactions. Heat is liberated in the reformer and the methanol synthesis reactors. The more efficient processes integrate the heat for distillation with the process waste heat, but even these processes must find a use for the excess process heat. Usually more steam is raised than is required for the process, and the excess may be exported or used to generate electrical power.

Figure 34 shows a typical methanol plant steam balance. High-pressure steam is generated downstream of the primary reformer, where the process temperature is the highest. The high-pressure steam is superheated in the convection



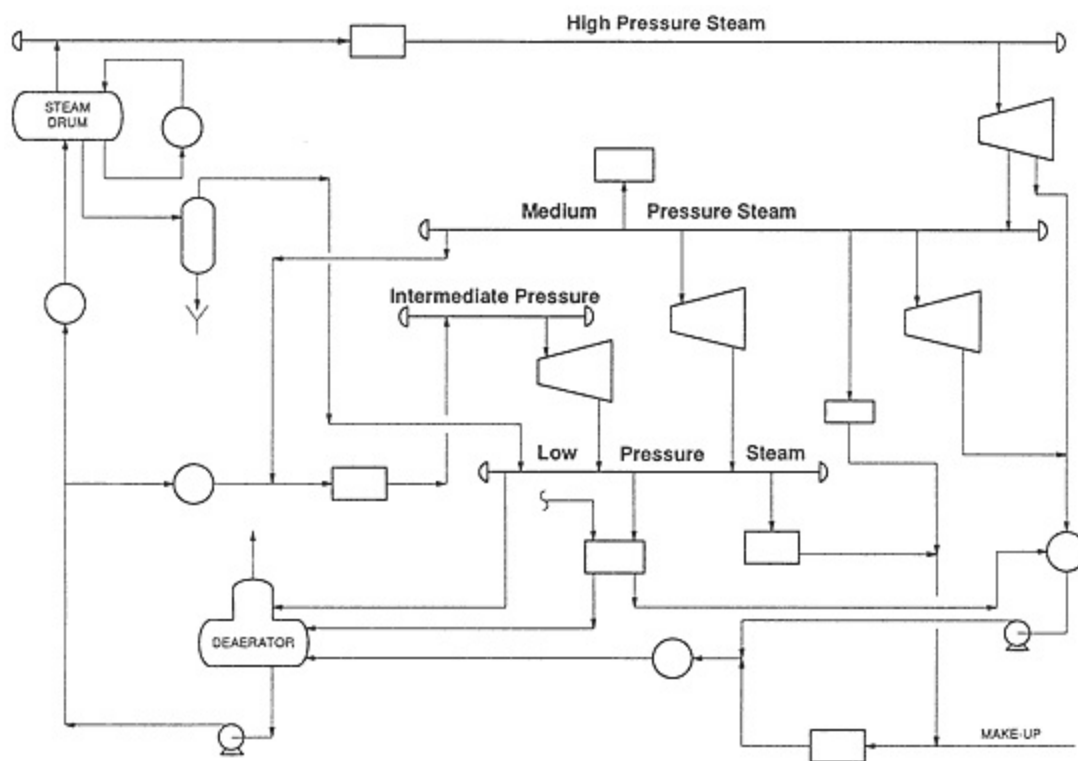


Figure 34  
Simplified methanol plant steam balance.  
(Courtesy of The M. W. Kellogg Company.)

section of the primary reformer, where the flue gases are the hottest. Work is extracted from this superheated high-pressure steam in the steam turbine driving the synthesis gas compressor as the steam pressure drops to the medium-pressure level. This medium-pressure steam is then used as process steam in the primary reformer as well as for other power requirements.

The third level of steam pressure is referred to as intermediate-pressure steam. Steam at this pressure may be generated between stages of the methanol reaction (for intercooled loops). The steam pressure is set to remove the heat of reaction while protecting the temperature-sensitive catalyst from excessively high temperatures. The lowest pressure steam is used to reboil the distillation columns. Most of the steam is condensed, polished, and recycled back to the deaerator. From the deaerator the boiler feedwater is heated by the process and used to make steam, once again completing the steam generation cycle. How the process heat and reformer flue gas heat are used has a significant effect on the efficiency of the process. In all modern processes the furnace thermal efficiency is 90+%. Additionally, the process heat generators are matched with heat users so that the overall process is highly efficient.

## 3.5

### Environmental Considerations for a Natural Gas Plant

#### 3.5.1

##### Effluents

The manufacture of methanol from natural gas using steam reforming is a relatively clean and environmentally safe process. Methanol is a chemical that is manufactured in large quantities, and compared with other chemical and petrochemical processes, the methanol process is not found to be a serious polluter. Despite a long record of clean operation, attention is being focused on all chemical manufacturing processes, including methanol. Table 9 lists the contaminants present in various effluents of a methanol plant.

CO<sub>2</sub> is generated in the reformer furnace combustion zone as natural gas is burned to produce the heat required for the endothermic reforming reaction. The reduction of CO<sub>2</sub> emissions is an environmental objective of modern methanol processes. By reducing CO<sub>2</sub> generation, the impact of methanol production on global warming can be reduced.

The flue gas from the reformer contains NO<sub>x</sub>, CO<sub>2</sub>, and occasionally volatile organic carbon (VOC) and particulates. Since the VOC and particulates are not present in any significant amount in a reformer using natural gas as fuel, they present no danger to the environment. CO<sub>2</sub> emissions are of concern and are directly related to the energy consumption of the process. Therefore, most of the effort to reduce CO<sub>2</sub> emissions parallels the effort to make the processes

Table 9 Contaminants from Various Sources in a Methanol Plant

Methanol plant effluents	Contaminants <sup>a</sup>
Reformer flue gas	NO <sub>x</sub> , VOC, particulates
Process condensate	TDS, TSS
Light ends	Ethers, ketones, aldehydes
Fusel oil	Methanol, higher alcohols
Process water	Methanol, heavy hydrocarbons, wax
Storage tank vent	Methanol
Spent catalyst	Various metals
Steam drum blowdown	TDS, TSS
Cooling tower blowdown	TDS, TSS
Surface water	Oil

<sup>a</sup> TDS, total dissolved solids; TSS, total suspended solids.

more energy efficient. NO<sub>x</sub> emissions, however, are not affected merely by the amount of fuel consumed. The amount of NO<sub>x</sub> generation is dependent on how the fuel is burned. Most plants in operation today control NO<sub>x</sub> by controlling NO<sub>x</sub>-forming compounds in the fuel. By using a clean fuel gas and controlled combustion, the NO<sub>x</sub> concentration in the flue gas remains low.

Process condensate collected from the front end of the plant is condensed steam and therefore quite clean except for traces of solids and a small amount of dissolved gases. The process condensate is stripped with steam and then sent to a demineralizer unit, where the solids are removed from the water so it can be recycled as boiler feedwater. The volatile by-products are carried with the steam into the reformer, where they are reprocessed.

At several points in the back end of the process, volatile by-products are removed. These light ends are combined and sent to the reformer to be used as fuel.

Fusel oil is taken off the refining column. It is comprised mostly of methanol and higher alcohols, which are easily burned as fuel in the reformer or a utility boiler. Generally, existing operations burn the fusel oil. With the current U.S. environmental regulations, specifically the Clean Air Act Amendment of 1990, fusel oil must be considered a hazardous waste, which makes it much more difficult to dispose of by burning.

Biological treatment breaks down methanol almost completely. Large quantities of methanol must be prevented from mixing with groundwater to avoid contamination of drinking water, but liquid effluents containing methanol can be biologically treated and oxidized to form methane and water [24].

One of the large-volume by-products of methanol manufacture is water (0.2 ton/ton), which is discharged from the bottom of the refining column. This water contains methanol and some higher alcohols, ketones, and paraffins. The refining column bottoms are skimmed or filtered to remove paraffins and then sent to a biological treatment unit, where the impurities are digested. The water effluent from the biological treatment unit is clean enough to be discharged into the surface water.

There are other effluents besides refining column bottoms from the manufacture of methanol. Effluents include steam system blowdown, surface water contaminated with oil, reformer flue gas, and the methanol storage tank vent.

The steam system blowdown contains dissolved solids but is clean and usually discharged directly to the surface water.

Area drains may contain oily water originating from oil drips and drains around the compressors and other lubricated machinery. Process spills of methanol can also make their way to the surface water around the plant. Typically the sewers in and around the plant are collected and discharged to a holding basin, where the surface water is analyzed before discharge.

In recent years, much more attention has been directed at methanol discharge to the atmosphere. This has resulted in improved schemes for capturing methanol vapor emissions from the atmospheric methanol storage tanks. Frequently the tank vent is scrubbed to absorb the methanol vapors, or the vapors are recompressed and the methanol condensed and returned to storage.

### 3.5.2 Alternative Treatments

Environmental regulations are changing rapidly toward less and less pollution in chemical plant effluents. This has led to alternative methods of processing and treating what once was discharged. Current environmental regulations in the United States require treating fusel oil as a hazardous waste. Thus a permit must now be issued to methanol manufacturers if they wish to burn fusel oil. Fusel oil burning was common in former designs. Modern designs have found alternative methods of disposing of fusel oil. One such design by Kellogg, shown in Fig. 35, separates the carbon-bearing components in a fusel oil stripper and recycles them to make more methanol product. The water and unremoved hydrocarbons are treated together with refining column bottoms.

Considerable attention has been given to the reformer stack and the NO<sub>x</sub> and CO<sub>2</sub> contained there. NO<sub>x</sub> can be removed at the source or removed after it is generated. Reduction can occur by lowering the combustion air temperature, eliminating or reducing the amount of purge gas burned, injecting steam into the combustion zone, or using "low-NO<sub>x</sub>" staged burners.





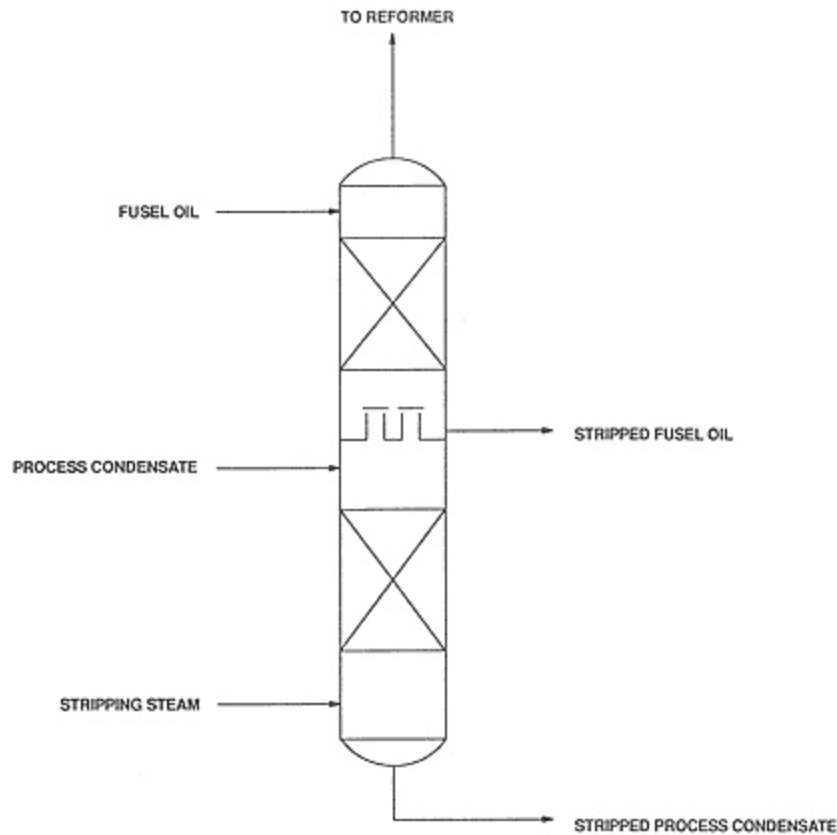


Figure 35

Kellogg unitized stripper for combined treatment of fusel oil and process condensate.  
(Courtesy of The M. W. Kellogg Company.)

Combustion modifications through changes in operating conditions and burner design are  $\text{NO}_x$  control techniques that have been successfully demonstrated on utility boilers and other stationary combustion sources. The reformer in most methanol plants operates at relatively low excess combustion air levels (1020%). Reducing emissions by further lowering excess air is not practical. However, burner redesign is a very effective means of controlling  $\text{NO}_x$ .

So-called low- $\text{NO}_x$  burners have been successfully demonstrated and have earned wide industry acceptance. Favored low- $\text{NO}_x$  techniques include staging the combustion air (Fig. 36) and staging the fuel (Fig. 37). Staged fuel is pre-

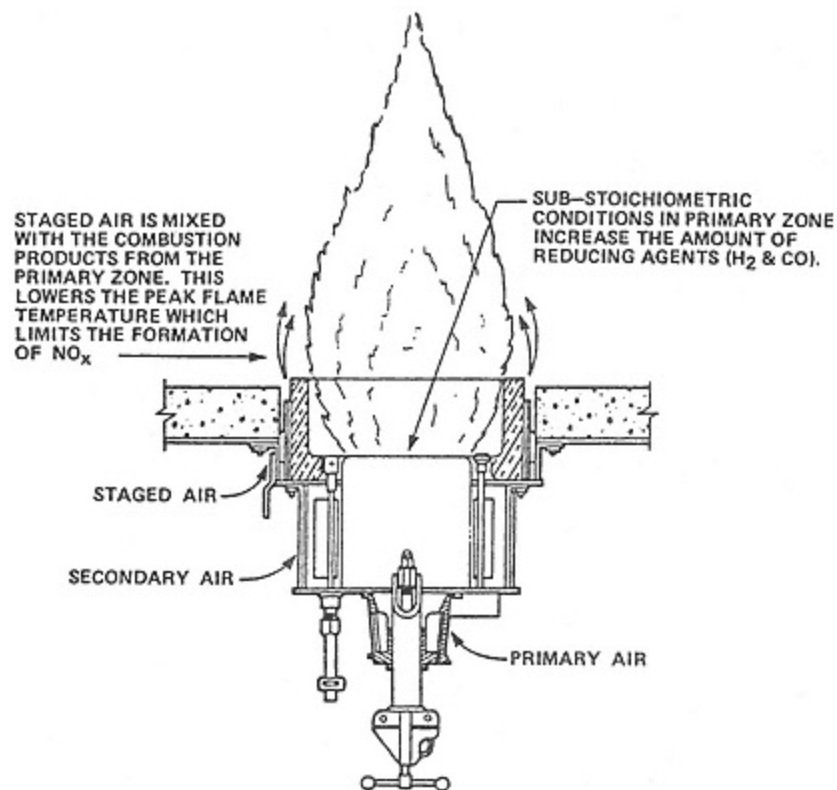


Figure 36  
Staged air burner.  
(Courtesy of the John Zink Company.)

ferred over staged air as the low- $\text{NO}_x$  burner design most widely adopted by burner vendors. By minimizing the peak flame temperature and controlling the nitrogen-oxygen contact in the hottest zones,  $\text{NO}_x$  formation can be significantly reduced.

The inherent drawback of any technique used to control  $\text{NO}_x$  emissions by lowering flame temperature is that  $\text{CO}$  emissions will increase. Using staged fuel, low- $\text{NO}_x$  burners, the  $\text{CO}$  concentration in the flue gas can be expected to rise. A  $\text{CO}$  concentration of 50100 ppmv in the flue gas is considered a good compromise with low- $\text{NO}_x$  burners.

If low- $\text{NO}_x$  burners cannot lower the  $\text{NO}_x$  to an acceptable level, selective catalytic reduction of the  $\text{NO}_x$  in the flue gas is an alternative method of treatment that converts the  $\text{NO}_x$  to nitrogen and water.

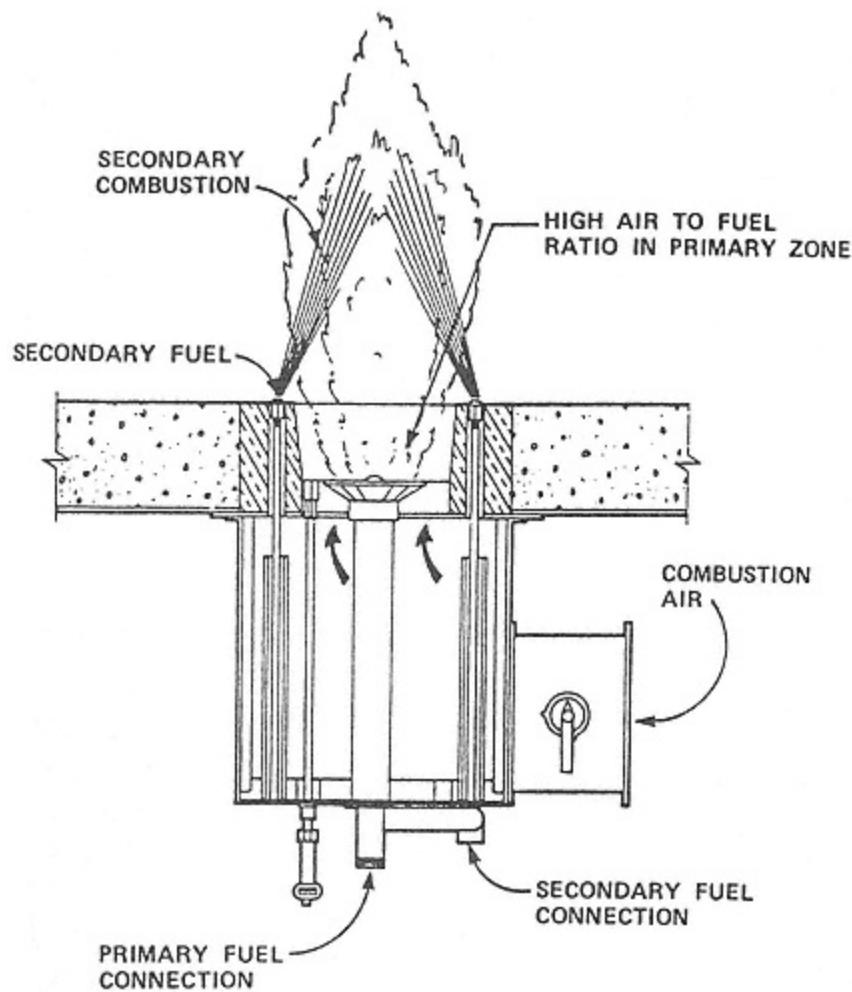


Figure 37  
Staged fuel burner.  
(Courtesy of the John Zink Company.)

Combined reforming, in which an autothermal reformer is used downstream of the primary reformer, is another means of reducing  $\text{NO}_x$  and  $\text{CO}_2$  generation: a portion of the reforming occurs in the autothermal reformer, where oxygen is consumed, and the duty on the primary reformer is reduced. Since the heat in the primary reformer is supplied by burning a hydrocarbon, natural gas, the reduction in fuel burned results in a reduction in  $\text{NO}_x$  and  $\text{CO}_2$  generated.

Once autothermal reforming is added to the process, the  $\text{NO}_x$  and  $\text{CO}_2$  generation can be reduced even further by incorporating a reforming exchanger. Heat exchange reforming uses the heat liberated in the autothermal reformer to provide the heat required in the primary reforming reaction without the need for burning fuel. See Section 3.3.5.

## 3.6

### Project Economics

Methanol producers compete in the commodity chemical business. Thus, their ability to produce the product at a cost-competitive price is essential. Any new methanol plant must deal with this issue, and by and large, the operator must approach a project with the intent of being a low-cost producer.

In this section both qualitative and quantitative data on the sensitivity to project economics are provided relative to major variables of natural gas cost, methanol price, capacity utilization, plant size, and plant cost.

### 3.6.1

#### Basis

The material presented here is based on using natural gas feed in a straight reforming process scheme for producing the synthesis gas needed for methanol production. Unless otherwise noted, the plant has a nameplate capacity of 750,000 tpy of U.S. grade AA methanol. Figure 38 shows such a complex.



Figure 38

Cape Horn Methanol 750,000 tpy methanol complex at Cabo Negro, Chile.  
(Photograph courtesy of The M. W. Kellogg Company.)

Capital cost can vary widely, depending on plant location, utility and off-site requirements, and infrastructure available or required. A U.S. Gulf Coast basis for costing is generally accepted in the petrochemical industry. This is the case here. Inherent in this position is the assumption of locating the plant at a developed site where only limited utilities and off-sites are required, such as cooling water system, demineralized water system, steam system, and product storage. For such a complex, the capital cost for the battery limits plant and limited off-sites, utilities, and storage facilities required in the 1993 time frame is about \$300 per annual metric ton installed capacity.

The operating staff for such a facility is shown in Figure 39. A total of 36 operating, administration, technical, and supervisory staff are shown. Such an operating staff is typical of this type of facility in the chemical and petrochemical industries.

The raw material and catalyst requirements typical of this 750,000 tpy methanol plant are as follows:

Natural gas, 7.8 Gcal (LHV)/t  
 Electrical power, 74 kWh/t  
 Cooling water makeup, 8.16 m<sup>3</sup>/t  
 Boiler feedwater makeup, 0.85 m<sup>3</sup>/t  
 Catalyst cost, \$1.60/t

Maintenance cost is generally represented as a percentage of the plant capital cost. For a methanol plant like that under consideration, the typical cost, including material and labor, is 2 1/23 1/2% per year.

### 3.6.2 Variable Analysis

In developing the data that follow, the following assumptions were made:

Complex consists of a battery limits plant with supporting off-sites, utilities, and storage. Battery limits methanol plant uses natural gas in a straight reforming process scheme. The complex is located at a developed site.

All financial analyses are based on 100% equity, 3 year project execution, and 15 year project life, and the internal rate of return is pretax.

### 3.6.3 Natural Gas Cost and Methanol Price

The data in Figure 40 present project profitability as a function of natural gas cost and methanol selling price. All gas costs are on an LHV basis.

The cost of natural gas at low methanol market prices has a significant effect on IRR. For example, at \$150/t for methanol, the IRR falls from 18.4%



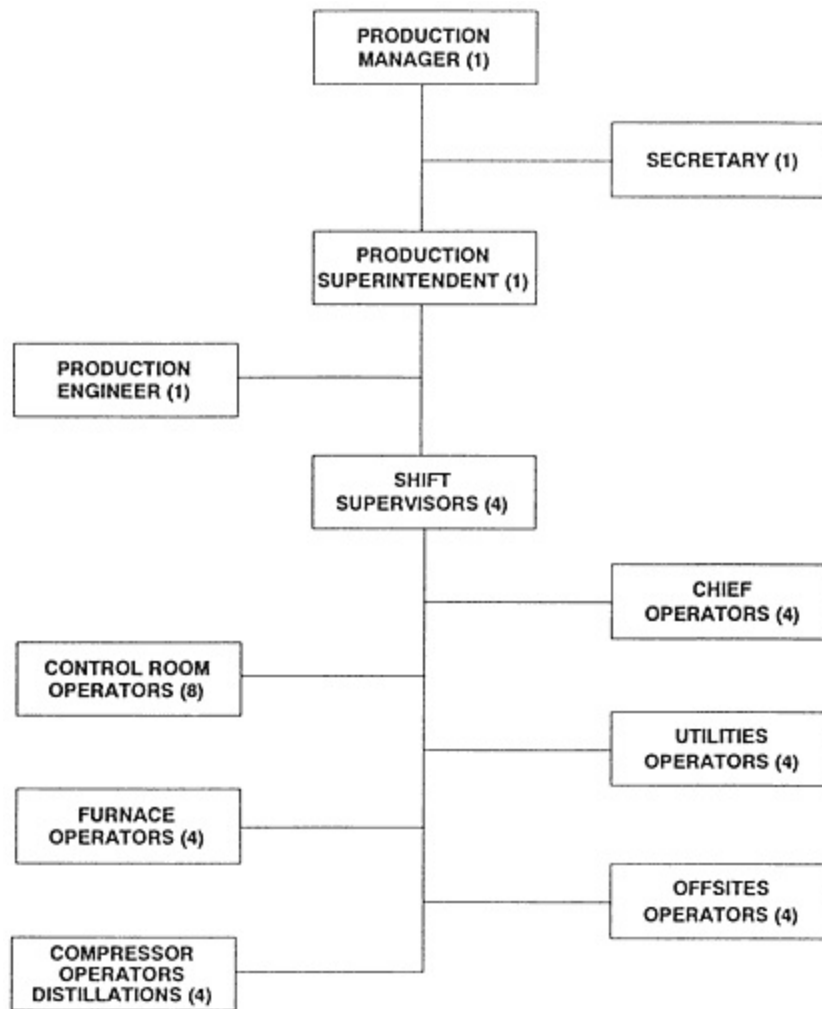


Figure 39  
Typical operating staff for a methanol plant facility.  
(Courtesy of The M. W. Kellogg Company.)

at a gas cost of \$1.50/MMBtu to 11.7% at a gas cost of \$2.50/MMBtu. At this level of gas cost and methanol price, an increase of \$1.00/MMBtu reduces the IRR by 6.7%. Thus, an increase of 66% in gas cost (from \$1.50 to \$2.50/ MMBtu) results in a reduction in project profitability of 35% (IRR drops from 18.4 to 11.7%).



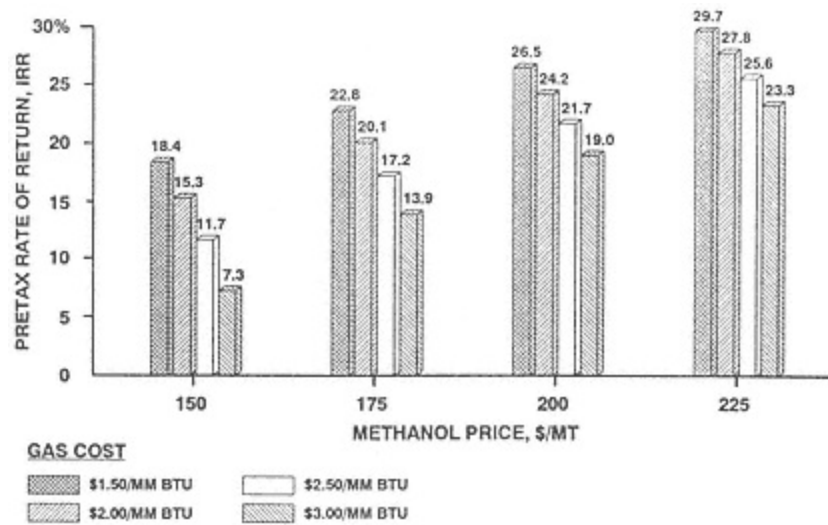


Figure 40  
Methanol plant profitability analysis. Sensitivity to gas cost and methanol selling price, 750,000 tpy plant size.  
(Courtesy of The M. W. Kellogg Company.)

As dramatic as these data are, the selling price of methanol is even more so. Using a natural gas cost of \$2.50/MMBtu and a methanol selling price of \$200/ t, the IRR is 21.7%. Relative to a methanol price of \$150/t, the IRR increases 10%. Here, a methanol price increase of some 33% increases project profitability by 85%.

With the data in Figure 40, one can make other differential analyses. The consistent conclusion is that the price of methanol is the significant factor in this feedstock cost and product price sensitivity analysis.

### 3.6.4 Capacity Utilization

Because methanol producers operate in the commodity market, they are particularly sensitive to product availability, which can directly affect product selling price. Thus, all new projects are undertaken to position the new plant operator as a low-cost producer. Gas cost, as we have seen, plays a large part in this overall approach. As such, many projects are placed in gas-rich areas of the world, which can mean a remote location.

What happens to project profitability as capacity utilizationplant reliabilitychanges is shown in Figure 41. These data are represented for a gas cost of \$2.00/MMBtu.

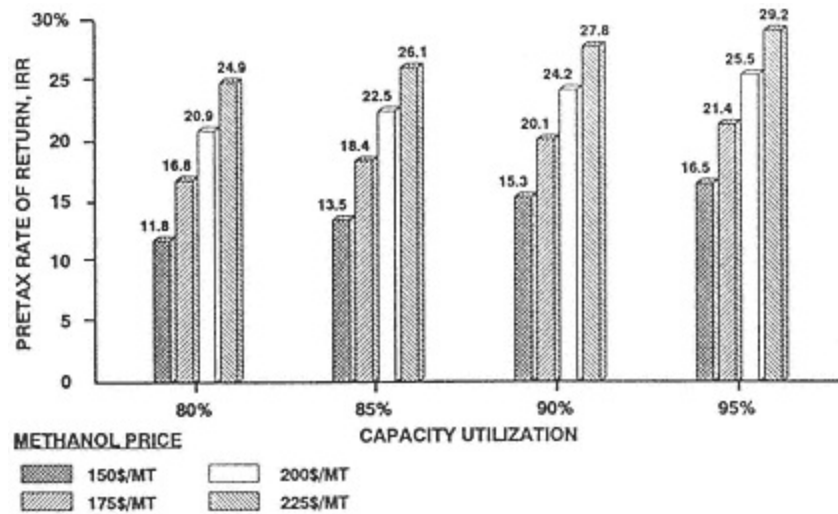


Figure 41  
Methanol project profitability analysis. Sensitivity to capacity utilization.  
Natural gas cost of \$2/MMBtu, 750,000 tpy plant size.  
(Courtesy of The M. W. Kellogg Company.)

In all the analyses presented in this chapter, a capacity utilization factor of 90% is used unless otherwise noted, as in Figure 41. It appears that currently the overall utilization factor for methanol plants on a global basis is around 85%, maybe slightly more. Some plants appear to have capacity utilization factors much lower, for example, 80% and less.

In a relatively low-price methanol market, the effect of plant reliability is particularly significant. From Figure 41, with methanol at \$150/t, the plant that operates at a 80% capacity utilization has an IRR of 11.8%; the plant that operates at a 90% capacity utilization has a 15.3% IRR. Increasing the reliability of the plant from 80 to 90% improves project profitability by about 30%.

When methanol prices are better, the change in IRR is less dramatic; however, the loss of potential profit is still significant. In addition to IRR data, net present value (NPV) data were also developed. NPV was computed at a 10% discount rate over the 15 year life of the project.

Following are NPV data for the 80, 90, and 95% capacity utilization plants at a selling price of \$200/t:

Capacity utilization (%)	NPVa \$000,000
80	199.4
90	279.1
95	317.4

a Millions of dollars, with gas cost at \$2/MMBtu and methanol at \$200/t.

The plant that achieves a 95% capacity utilization has an NPV of \$317,400,000 on the same basis. Again, relative to the less reliable 80% capacity utilization plant, this represents a significant increase of about 59%.

These data lead to a clear conclusion: plant reliability is essential in positioning the operator to be a low-cost producer and in maximizing profits.

### 3.6.5 Plant Size

Thus far we have considered a large-scale plant of 750,000 tpy. Plants of about this size are about the largest in operation today. Smaller plant sizes for some projects are being considered. In general, however, there is a price to pay for smaller plants in the chemical process industries, and methanol is no exception.

Figure 42 shows the project profitability sensitivity for plant sizes of 250,000, 500,000, and 750,000 tpy. These data were developed for a gas cost of \$2/ MMBtu. These data show that plant size for a given methanol price dramatically affects profitability. The smaller 250,000 tpy plant has an IRR of 13.6% with methanol at \$200/t; the larger 750,000 tpy plant has an IRR of 24.2% at the same methanol price. Changing from the smallest to the largest plant improves project profitability by about 80%. Clearly, there must be special circumstances to warrant the small plant. There may be such reasons as market size, distribution system, plant location, and captive use that lead to a small plant project.

Figure 43 is a reorganization of the data in Figure 42 to a format that can be used to give the small plant investor a quantitative understanding of selling price disadvantage relative to the larger plants. For example, if one assumes a constant IRR of 15%, the selling price of methanol from the 750,000 tpy plant is about \$149/t; for the 250,000 tpy plant the selling price is about \$212/t. Thus the smaller plant has a selling price disadvantage of some \$63/t. If the smaller plant operator will compete on a free market basis, this disadvantage must be overcome. Gas price is a consideration; for the complex considered here, \$1.00/ MMBtu change in gas cost, if passed through to methanol price, has an impact

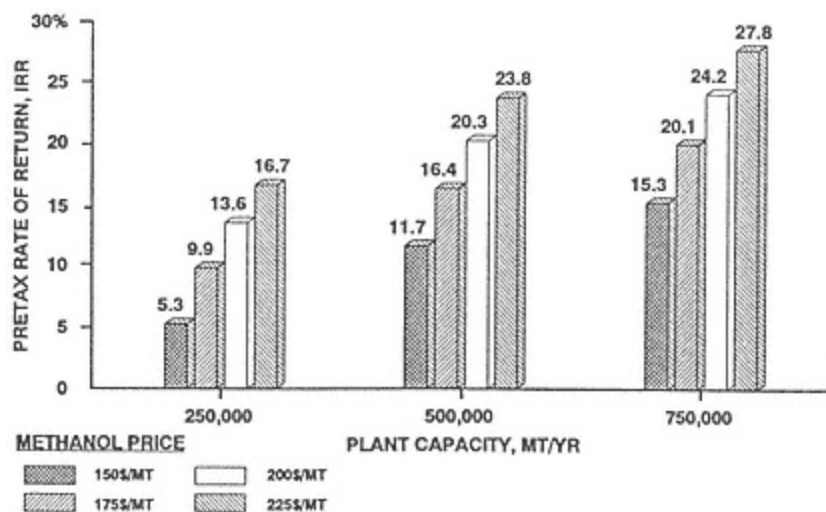


Figure 42  
Methanol project profitability analysis. Sensitivity to plant size.  
Natural gas cost of \$2/MMBtu.  
(Courtesy of The M. W. Kellogg Company.)

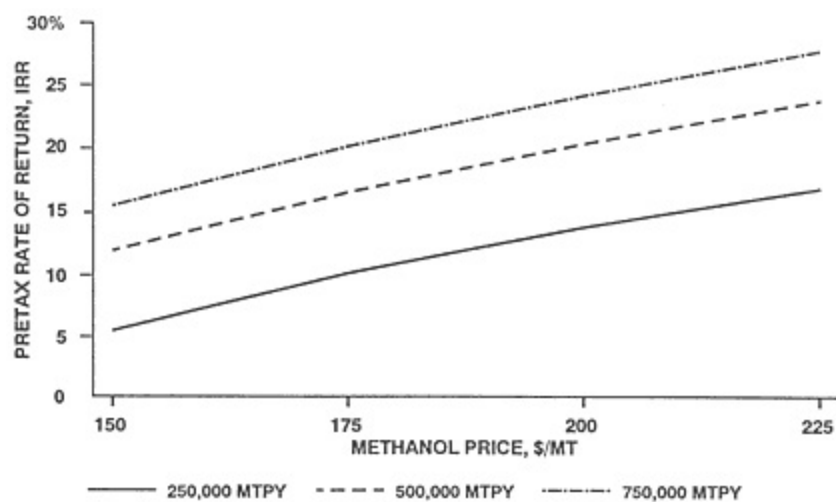


Figure 43  
Methanol project profitability analysis. Sensitivity to plant size. Natural gas  
cost of 2/MMBtu.  
(Courtesy of The M. W. Kellogg Company.)

of about \$30/t. Transportation and distribution are other items that can play important roles.

The data show rather clearly, however, that on the same basis, the smaller plant is at a significant disadvantage competing in the marketplace.

### 3.6.6

#### Plant Capital Cost

One of the most significant factors affecting plant capital cost is location. Capital cost is influenced by whether the site is developed or grass roots. Developed sites generally have basic utilities, such as electrical power and water. Grass roots sites typically require the inclusion of such utility systems for the project. Additionally, at some grass roots and undeveloped sites, there is little or no local infrastructure to support the construction activity. A construction camp may be required, as well as imported construction labor. Alternatively, the project can adopt modular construction to offset the need for a large construction force.

These factors can significantly affect plant cost. Depending on project specifics, location factor can in some instances lead to an increase of as much as 60% in plant cost.

For a methanol plant sited in a gas-rich area that is not developed, the increase in plant cost affects project profitability. The data in Figure 44 show the sensitivity of plant cost on project IRR. For example, with a gas cost of \$2.00/ MMBtu, a \$175/t selling price for methanol, and plant cost of 100, 120, and 140%, the project IRR are 20.1, 16.9, and 14.3%, respectively. However, the incentive to locate at a gas-rich undeveloped site is generally that the cost for natural gas is relatively low.

Data from Figure 44 can be used to develop a quantitative understanding of what the relatively low gas cost and high plant cost do to project profitability.

A way of making such an analysis is to consider projects at sites where the plant cost is 100, 120, and 140%, IRR at 15%, and a methanol selling price of \$175/t and determine the corresponding gas cost. For this example the results are as follows:

Plant cost (%)	Natural gas cost (\$/MMBtu)
100	2.85
120	2.35
140	1.85

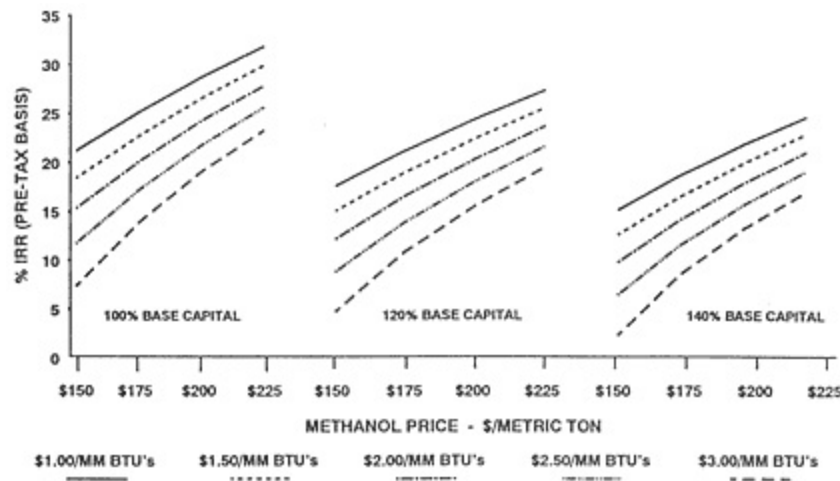


Figure 44  
Methanol project profitability analysis. Sensitivity to plant cost.  
(Courtesy of The M. W. Kellogg Company.)

Thus the plant operator at the developed site (100% plant cost) can compete with the operator with the plant costing 140% at a \$1.00/MMBtu cost disadvantage for natural gas (\$2.85 to \$1.85/MMBtu).

If one considers that the operator at the remote site may have additional costs, such as increased shipping and possibly import duties, this "gate price" is effectively reduced. Assuming that these additional cost factors amount to \$25/t, then the gate price for this methanol in the preceding example is  $\$175 - \$25 = \$150/\text{t}$ . At 120 and 140% plant cost and \$150/t methanol price, with an IRR of 15%, the corresponding natural gas cost is about \$1.55 and \$1.05/MMBtu, respectively.

Thus, the operator at the developed site (100% plant cost) could compete with a gas cost disadvantage of  $\$2.85 - \$1.55/\text{MMBtu} = \$1.30/\text{MMBtu}$  and  $\$2.85 - \$1.05/\text{MMBtu} = \$1.80/\text{MMBtu}$  relative to the operators at the remote with 120 and 140% plant costs, respectively.

There is a significant message here: with plants in remote locations costing more and having additional costs to contend with relative to the plant at a developed site, the operator of the plant at the developed site close to market can incur a significant natural gas cost disadvantage and compete on a free market basis.

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## 4

## Methanol to Gasoline and Olefins

Clarence D. Chang

Mobil Research and Development Corporation, Princeton, New Jersey

## 4.1

## Conversion of Methanol to Gasoline

The Mobil methanol-to-gasoline (MTG) process is one of two current commercial technologies for producing synthetic fluid fuels from synthesis gas. Until 1985, the sole "synfuel" process in commercial practice was the Sasol Process (in South Africa), which is based on classic Fischer-Tropsch chemistry and utilizes coal-derived synthesis gas. The Sasol process produces a wide range of aliphatic hydrocarbon products, from light paraffins to waxes, whose carbon number distribution is governed by Schulz-Flory kinetics. The MTG process, conceived and developed in the wake of the 1973 Arab oil embargo, is utilized in New Zealand for conversion of natural gas, via methanol, to a regular unleaded gasoline composed mainly of isoparaffins and aromatics and low in benzene and sulfur. Known there as the GTG (gas-to-gasoline) process, the New Zealand facility was designed to meet one-third of that country's demand for transportation fuel, thereby lessening their heavy dependence on foreign oil imports.

The chemical basis of the MTG process [1,2] is the direct conversion of methanol to hydrocarbons, catalyzed by the synthetic zeolite ZSM-5 [35]. The overall stoichiometry of the reaction is



where  $(CH_2)_n$  represents the average formula of the hydrocarbon mixture produced. This mixture is composed of olefins, aromatics, and paraffins. Since no net hydrogen is made in the MTG reaction, stoichiometry dictates that for every aromatic ring formed, 3 mol hydrogen must be transferred in concurrent paraffin formation (via saturation of olefins).

#### 4.1.1

#### The MTG Catalyst

##### 4.1.1.1

##### Composition and Structure

Although many catalysts with the capability of converting methanol to hydrocarbons have now been identified, the synthetic zeolite ZSM-5 is the most selective and stable catalyst discovered to date. Catalysts active for the MTG reaction are all Brønsted acids.

Zeolites are crystalline aluminosilicates having the empirical formula



where M is an exchangeable cation with valence n and  $x > 2$ . The zeolite crystal framework is three-dimensional and is composed of  $TO_4$  tetrahedra interconnected through sharing of oxygen atoms at their vertices. The tetrahedral central ion T may be Si or Al, with the proviso (Loewenstein's rule) that Al-O-Al linkages be avoided. This results in a negatively charged framework, with association cations M necessary for electroneutrality. When M is a proton, the zeolite is a Brønsted acid. It is noted in passing that framework T atoms may be subject to isomorphous substitution, such as Si for Al or Ga for Al [611].

##### 4.1.1.2

##### Shape Selectivity

Zeolites of catalytic utility are microporous. Such materials are permeated by channels and cages of molecular dimensions (513 Å). The interior of the zeolite is accessed via pores having various well-defined geometrics. As a result, intracrystalline sorption can be highly selective depending on sorbate size and shape. This phenomenon is known as "molecular sieving" or "shape selectivity." When catalytic sites are present in the zeolite, "shape-selective catalysis" [1214] can occur.

The zeolite ZSM-5 is characterized by pore openings consisting of 10 rings of oxygen atoms and an intersecting channel system of straight and sinusoidal channels. The pores associated with the two channel systems have slightly different geometry. This is shown in Figure 1, which also compares ZSM-5 pores with 8-ring and 12-ring pores from zeolites erionite and faujasite, respectively. Figure 2 gives a representation of the ZSM-5 pore system, and Figure 3 provides stereoscopic views of the crystal structure.

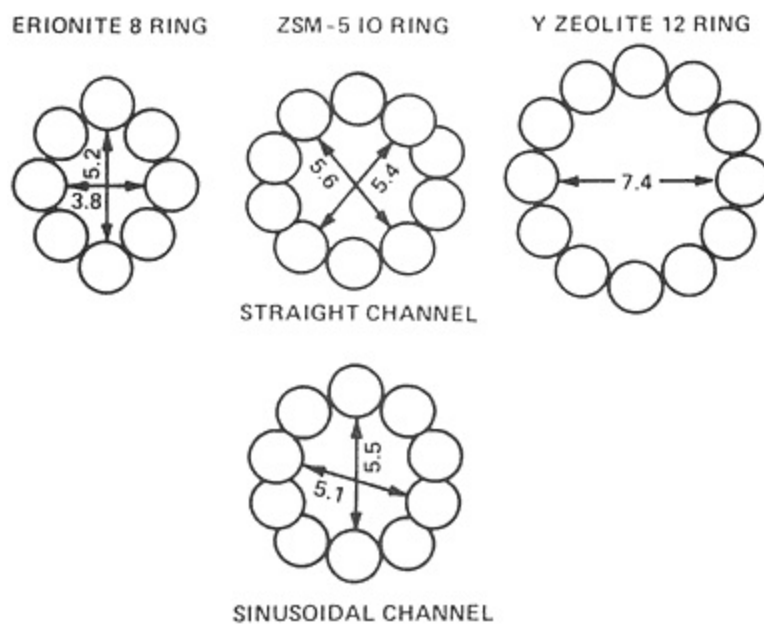


Figure 1  
Pore geometries of typical 8-, 10-, and 12-ring zeolites.

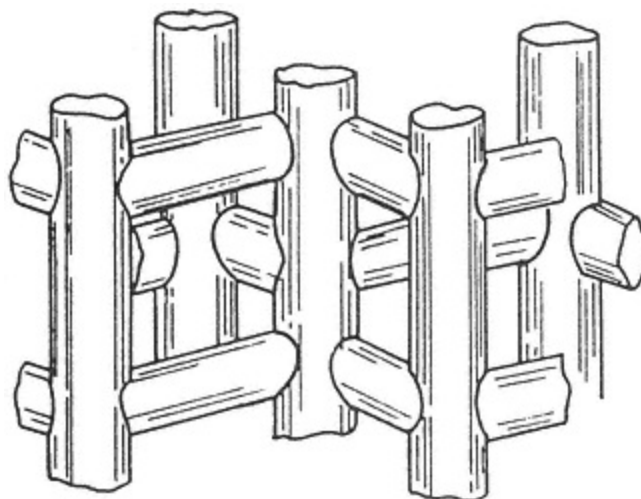


Figure 2  
The ZSM-5 pore system.

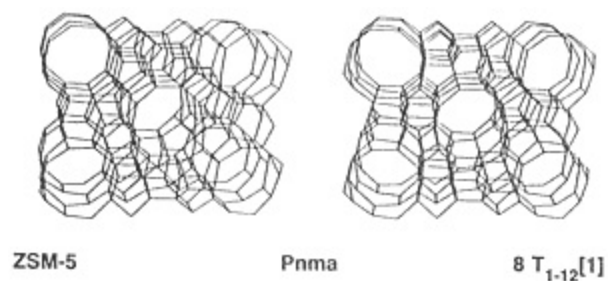
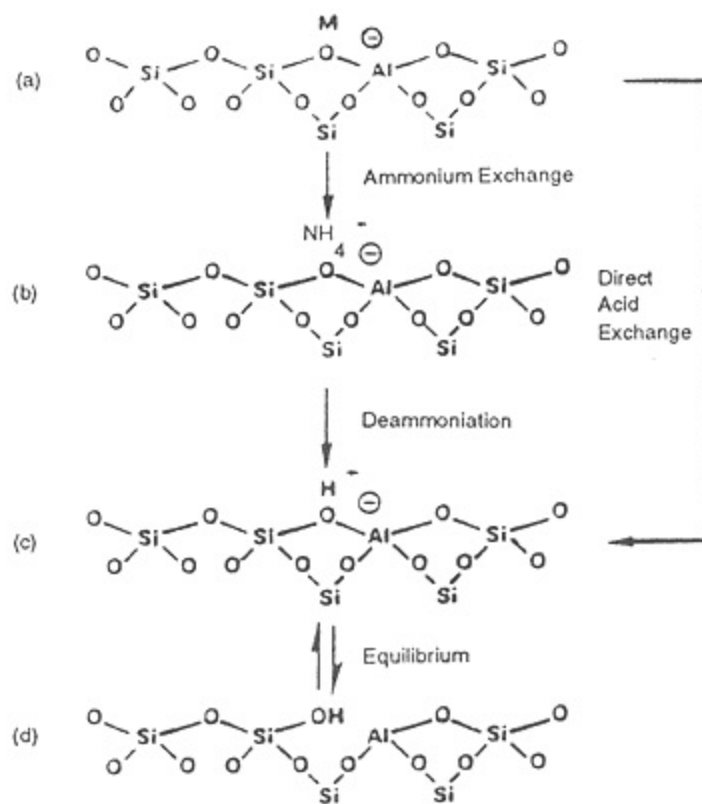


Figure 3  
Stereo-pair drawing of the ZSM-5 framework viewed along [010].  
(From Ref. 5.)



Scheme 1

Owing to its pore geometry, ZSM-5 is shape selective. It admits normal and single methyl branched paraffins and can discriminate between certain aromatics depending on their size and shape. For example, the diffusivity of p-xylene in ZSM-5 is 10<sup>3</sup> higher than that of the ortho and meta isomers at ambient conditions [15].

#### 4.1.1.3

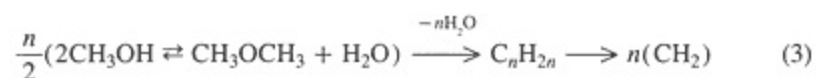
##### Nature of the Active Site

As indicated, zeolites possess exchangeable cations and therefore can exist as protonic acids. The H-zeolite can be generated either by direct hydronium exchange with mineral acids or by thermolysis of an NH<sub>4</sub><sup>+</sup> precursor [16]:

#### 4.1.2

##### MTG Reaction Pathway

The MTG reaction path is illustrated in Figure 4[1], which shows the variation in product selectivity with contact time at 370°C and 1 atm. The reaction path may be summarized as follows:



where (CH<sub>2</sub>) = average formula of a paraffin-aromatic mixture, from which it is seen that the reaction is sequential and complex. The initial stage is a rapid dehydration to an equilibrium mixture of dimethyl ether (DME), water, and methanol. Further loss of water affords light olefins, which subsequently undergo various reactions, including oligomerization, cyclization, and H transfer to yield an aromatic-paraffin mixture. From Figure 4, it is apparent that under the stated conditions these various reactions are kinetically coupled.

Although the mechanism of aromatics (and concurrent paraffin) formation from the intermediate olefins can readily be understood in terms of classic carbenium ion theory, the mechanism of formation of the initial C-C bond from C<sub>1</sub> precursors remains a mystery and a matter of controversy at present. Unlike other alkanols, methanol lacks a β-H and therefore cannot undergo the expected elimination reaction yielding water and a parent olefin. Much of the controversy is centered on the genesis, nature, and fate of the reactive "C<sub>1</sub> moiety." For a discussion the reader is referred to several reviews on the subject [2,79].

#### 4.1.3

##### Thermochemistry

The MTG reaction is highly exothermic. This is demonstrated in Figure 5 [1], where the heat release associated with the data in Figure 4 are plotted. The degree of exothermicity depends on the conversion as well as the product composition.



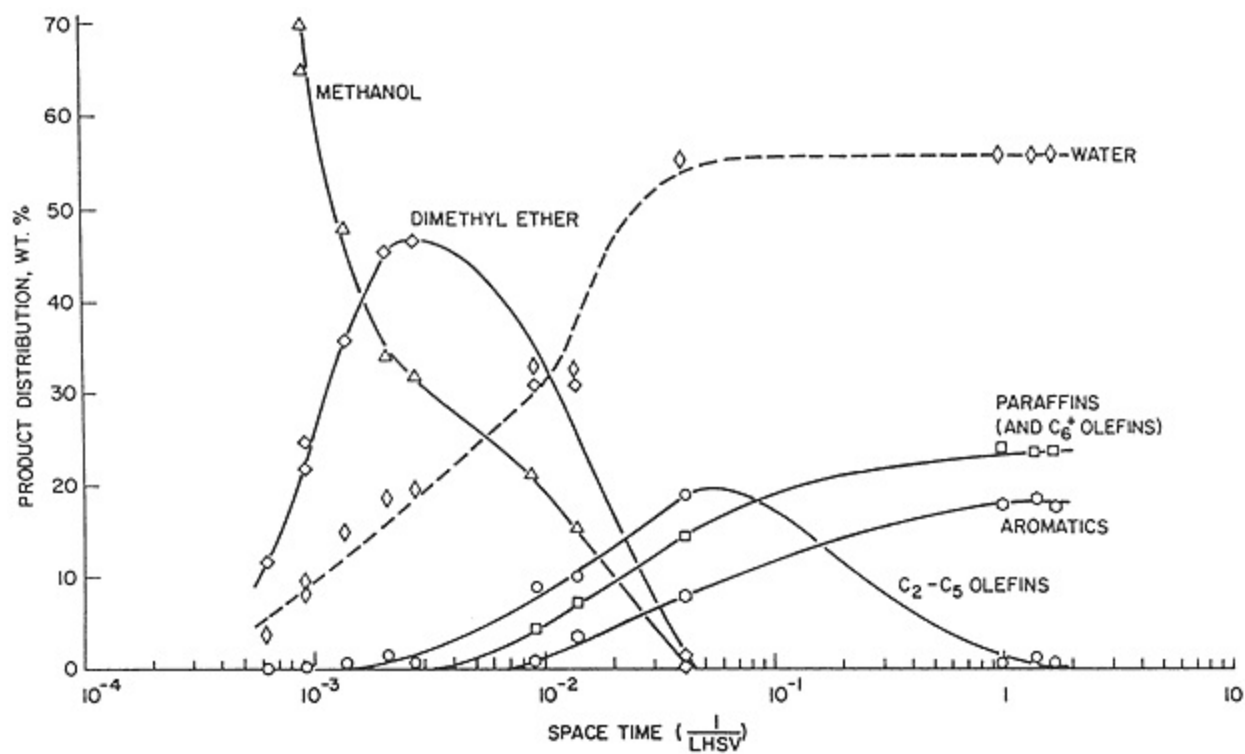


Figure 4  
The MTG reaction path at 370°C, 1 atm.  
(From Ref. 1).



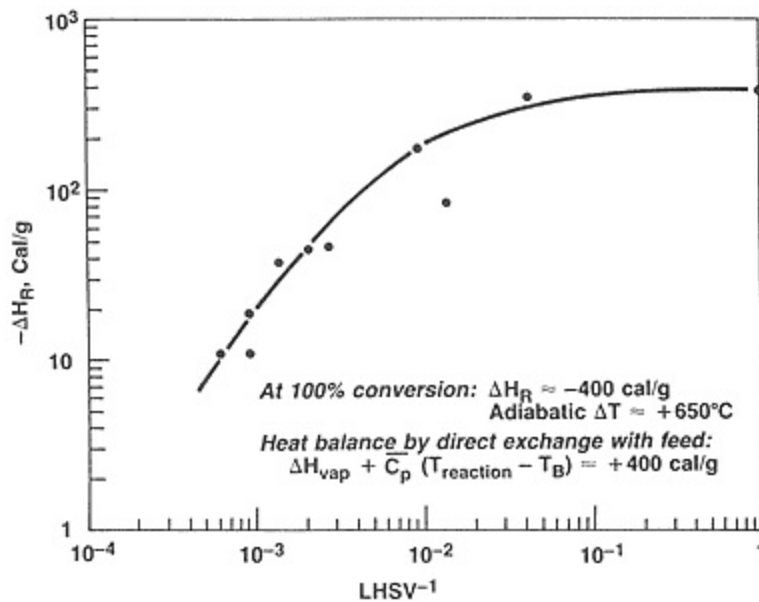


Figure 5  
 Heat of reaction at 370°C, 1 atm, as a function on contact time.  
 (From Ref. 1.)

In Figure 6[2], heats of reaction are plotted against C number for typical MTG hydrocarbon products. At complete methanol conversion,  $\Delta H = 400$  cal/g, which would result in an adiabatic temperature rise of  $\sim 650^\circ\text{C}$ . Fortunately, the sum of the heat of vaporization of methanol and the sensible heat required to bring methanol to the reaction temperature balances the heat of reaction, as indicated in Figure 5. This is important for process design and optimization.

#### 4.1.4 Hydrocarbon Product Distribution

Shown in Table 1 [1] is a typical MTG hydrocarbon product analysis. The selectivity can of course be varied by changing reaction conditions, as shown later. The hydrocarbon distribution displays some noteworthy features: little or no hydrogen, methane, or ethane is produced; the carbon number range is limited mainly to C<sub>3</sub>C<sub>10</sub> (it is fortuitous that C<sub>10</sub> is also the normal end point of conventional gasoline); the C<sub>5</sub> fraction contains significant amounts of isobutane, which will be useful for alkylate synthesis under conditions in which light olefins are brought into balance with isobutane; and the aromatics are nearly exclusively methyl substituted.

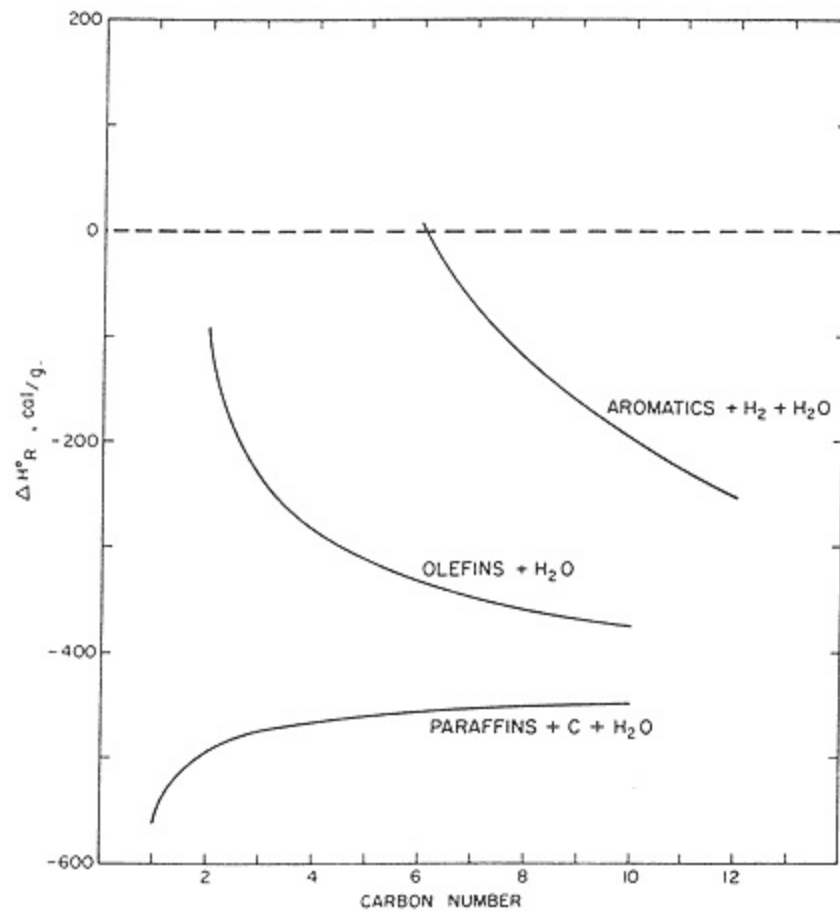


Figure 6

Heats of reaction in the formation of select hydrocarbons from methanol at 600 K.  
(From Ref. 2.)

The typical MTG aromatics distribution is shown in detail in Table 2 [1], along with the calculated (normalized) thermodynamic equilibrium values. The xylenes are seen to be essentially at equilibrium, but departure from equilibrium distribution becomes more pronounced with higher aromatics.

A characteristic aromatic constituent of ZSM-5-catalyzed MTG is durene (1,2,4,5-tetramethylbenzene), which is the predominant C<sub>10</sub> aromatic, although it is not the thermodynamically favored tetramethylbenzene isomer. This is a consequence of catalyst shape selectivity, wherein the more bulky isomers can-

Table 1 Typical MTG Hydrocarbon Distribution

Reaction conditions	
T, °C	371
LHSV, hr <sup>-1</sup>	1.0
Conversion, %	100.0
Hydrocarbon distribution, wt%	
Methane	1.0
Ethane	0.6
Ethylene	0.5
Propane	16.2
Propylene	1.0
i-Butane	18.7
n-Butane	5.6
Butenes	1.3
i-Pentane	7.8
n-Pentane	1.3
Pentenenes	0.5
C6+ aliphatics	4.3
Benzene	1.7
Toluene	10.5
Ethylbenzene	0.8
Xylenes	17.2
C9 aromatics	7.5
C10 aromatics	3.3
C <sub>11</sub> + aromatics	0.2

Source: From Reference 1.

not diffuse through the pore. It is believed that these isomers are trapped in the more spacious channel intersections and must isomerize to the symmetrical isomer before they can escape. Evidence in support of this view may be found in the work Schulz et al. [20], who used HF to dissolve ZSM-5 after MTG reaction, extracted the residue with CH<sub>2</sub>Cl<sub>2</sub>, and identified polyalkyl aromatics, mostly mononuclear, but too bulky to exit the zeolite pores ("ship-in-the-bottle" effect), and Anderson and Klinowski [21], who found by <sup>13</sup>C nuclear magnetic resonance, significant amounts of intracrystalline durene during MTG reaction. The accumulation of higher aromatics in the zeolite channel intersections may therefore be a major contributor to reversible catalyst aging.

Since durene is a solid under ambient conditions (melting point 79.3°C), it was determined based on driveability tests and marketing factors that it would be preferable to reduce its content to < 5% in the finished gasoline even though

Table 2 Typical Aromatics Distribution (normalized) in MTG Hydrocarbons

	Normalized distribution (wt%)	Approach to equilibria <sup>a</sup>
Benzene	4.1	
Toluene	25.6	
Ethylbenzene	1.9	
Xylenes		
Ortho	9.0	0.90
Meta	22.8	1.04
Para	10.0	1.02
Trimethylbenzenes		
1,2,3	0.9	0.82
1,2,4	11.1	1.19
1,3,5	2.1	0.57
Ethyltoluenes		
Ortho	0.7	
Meta + para	4.1	
Isopropylbenzene	0.2	
Tetramethylbenzenes		
1,2,3,4	0.4	0.58
1,2,3,5	1.9	0.87
1,2,4,5	2.0	1.39
Other A10b	2.7	
A <sub>11</sub> <sup>+</sup>	0.4	

<sup>a</sup> Ratio of observed to equilibrium values (normalized) at 370°C.

<sup>b</sup> Diethylbenzenes + dimethyl ethylbenzenes.

Source: From Reference 1.

its octane rating is high [22]. In the New Zealand plant (see later) this is accomplished by hydrofinishing the heavier gasoline fractions. Higher durene concentrations may be tolerable in warmer climates or in cars equipped with fuel injection.

#### 4.1.5

#### Kinetic Parameters

##### 4.1.5.1

##### Pressure Effects

The main effect of varying feed partial pressure is to change the relative rates of olefin formation and aromatization. Reducing pressure decouples the two reactions; increasing pressure enhances their overlap. This phenomenon is represented in Figure 7 [23], where the shaded areas highlight the extent of over-

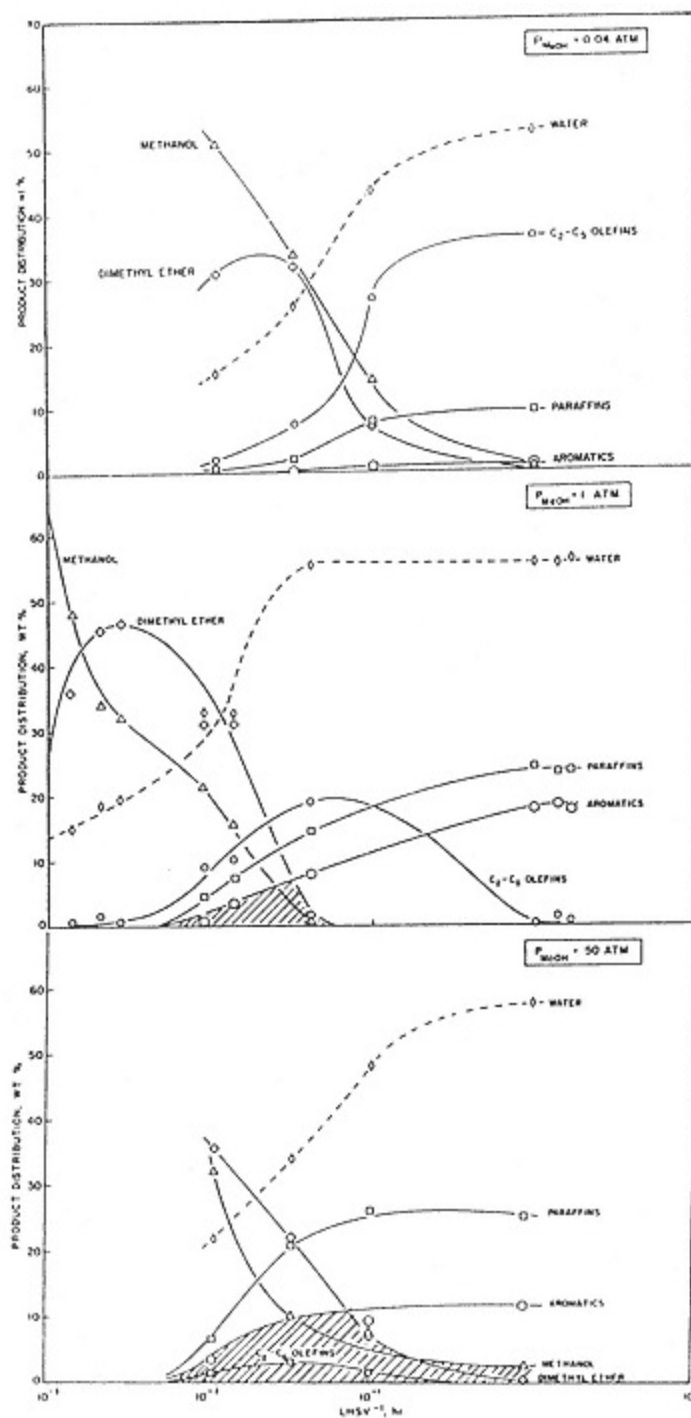


Figure 7  
Effect of pressure at 370°C on the MTG reaction path.  
(From Ref. 25.)

lap of the methanol and DME consumption and aromatics formation trajectories. It is in the region of overlap that the potential for ring methylation is highest, and the tendency is toward exhaustive methylation. Thus increasing pressure increases durene selectivity, as seen in Figure 8 [23]. Again, since durene is the bulkiest polymethylbenzene that can readily diffuse through the ZSM-5 pore, it is the most abundant A<sub>10</sub> product isomer.

#### 4.1.5.2 Temperature Effects

In the presence of ZSM-5, the MTG reaction "initiates" at above 250°C. Below this threshold temperature the main reaction is methanol dehydration to DME. Under isothermal conditions the effect of temperature (at low space velocity) is illustrated by Figure 9 [1], which demonstrates that with changing temperature the pathway of Equation (2) is tracked. However, above about 450°C light olefins and methane appear. At these low space velocity conditions methane is the result of secondary cracking, and increased olefins can be attributed to secondary cracking and/or differences in activation energy [24] between their formation and subsequent aromatization. Above 500°C, CH<sub>4</sub> and CO from methanol dissociation become detectable.

#### 4.1.5.3 Effect of Catalyst SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

The zeolite ZSM-5 is one of a small number of zeolites that can be synthesized with a wide range of Al content, including its pure silica form, and therefore

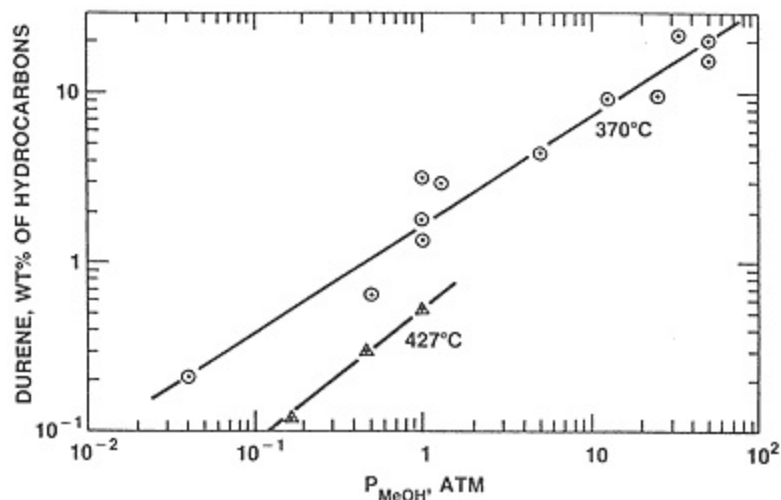


Figure 8  
Effect of pressure on durene formation at 1.01.2 h and 1 LHSV.  
(From Ref. 23.)

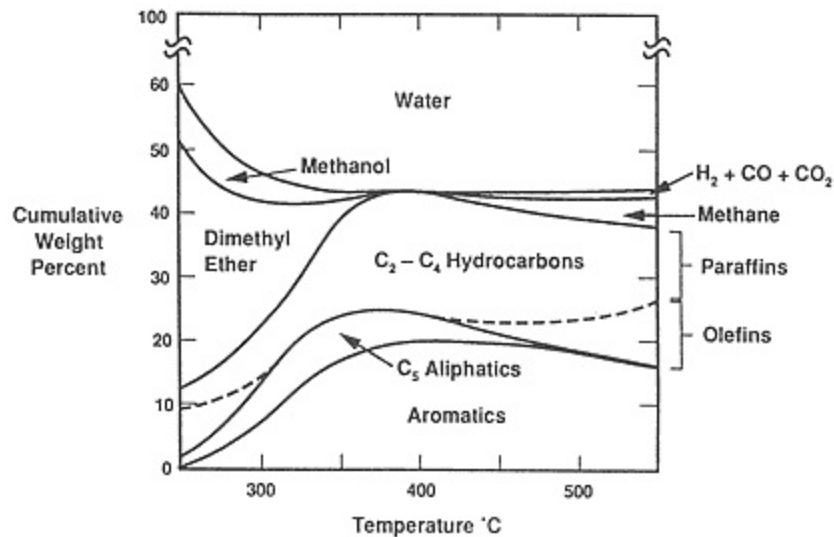


Figure 9

Effect of temperature on product distribution of 0.60.7 h 1 LHSV, and 1 atm.  
(From Ref. 1.)

displays wide range of activity. The effect of increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (decreasing acid concentration) at constant temperature, pressure, and contact time is equivalent to moving backward along the MTG reaction path. Thus, the product becomes increasingly olefinic until the appearance of methanol and DME. Typical data are plotted in Figure 10 [24].

At high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ( $> 70$ ) and with suitable adjustment of reaction temperature and contact time to provide complete conversion, it has been found possible substantially to decouple olefin formation from aromatization. This mode of operation is the basis of the methanol-to-olefins (MTO) process (see later).

#### 4.1.5.4

#### Catalyst Aging and Regeneration

Unlike most zeolites, ZSM-5 is stable to severe steaming conditions, such as those encountered during MTG service. Although ZSM-5 undergoes slow deactivation, it is readily reactivated by air calcination to remove accumulated organic deposits.

In fixed-bed reactors, the MTG catalyst ages via a "band-aging" mechanism [25,26]. In this type of aging, a zone, or band, where most of the reaction is occurring, travels slowly toward the reactor exit, leaving behind an increasing mass of deactivated catalyst. As the band nears the end of the catalyst bed, the product becomes more olefinic and less aromatic until methanol breakthrough occurs, signaling the end of cycle and the need for regeneration. These chang-

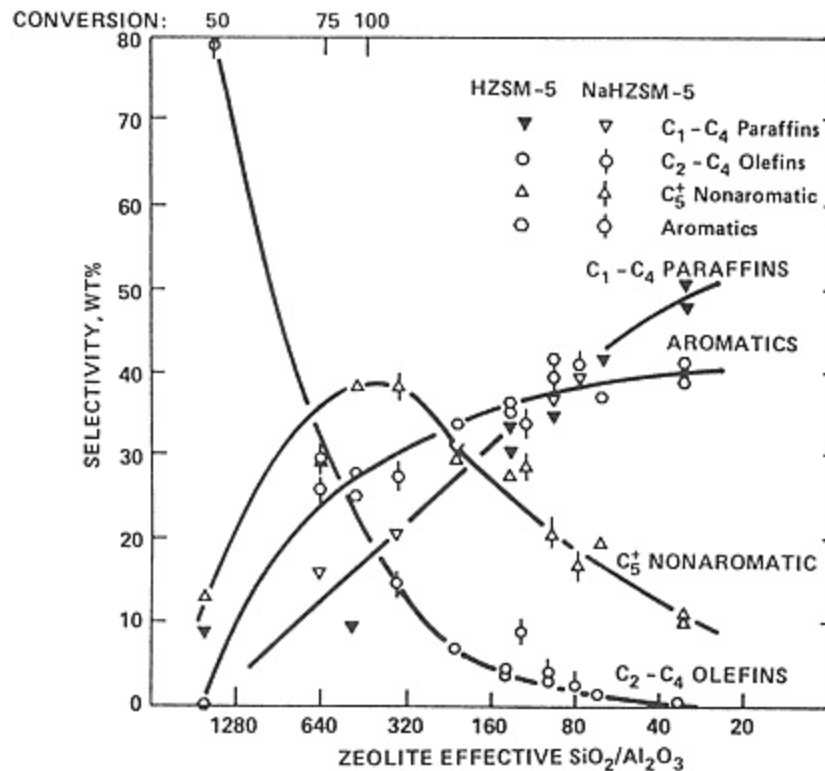


Figure 10

Variation of hydrocarbon selectivity with ZSM-5-effective  $\text{SiO}_2/\text{Al}_2\text{O}_3$  at  $370^\circ\text{C}$ , 1 h, and 1 LHSV.  
(From Ref. 24.)

es in selectivity can be interpreted as follows: as the volume of active catalyst diminishes owing to band aging, the effective contact time decreases, equal to moving backward on the reaction path represented in Equation (3).

#### 4.1.6 Kinetic Modeling

Kinetic analysis of the complex MTG reaction is somewhat simplified by the finding (Fig. 11) [2] that the methanol-DME-water equilibrium (dashed curves) is rapidly established and maintained along the initial segment of reaction path. Experimental data in Figure 11 demonstrate that this holds for pure methanol as well as pure DME feed. Thus oxygenates can be treated as a single pseudospecies or kinetic "lump." Kinetic analysis can be further simplified by



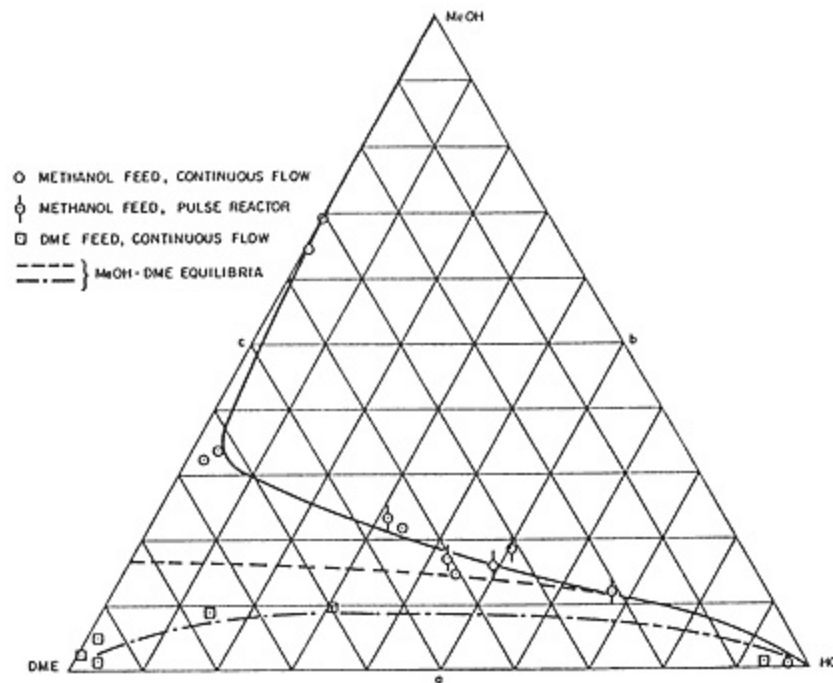


Figure 11  
Approach to methanol/DME/H<sub>2</sub>O equilibrium at 370°C, 1 atm  
(dashed lines are equilibrium).  
(From Ref. 2.)

regarding olefins as single lumps and lumping together paraffins and aromatics. In this scheme all lumps, including methanol and DME, are treated as  $(\text{CH}_2)_n$ , that is, on a water-free basis [this is already implicit in Eqs. (1) and (2)].

The autocatalytic nature of the early steps of the MTG reaction was first recognized by Chen and Reagan [27], who proposed the following simple lumping scheme:



where A = oxygenates, B = olefins, and C = aromatics + paraffins.

Neglecting  $k_3$  at low conversions, the reaction rate is given by

$$-\frac{dA}{dt} = k_1A + k_2AB \quad (5)$$

which integrated yields

$$k_2 = \frac{1}{(1+R)t} \ln \frac{(R+B)A_0}{RA} \quad (6)$$

where  $R = k_1/k_2$ . Experimental data were fit for  $k_1 = 0.02$  and  $k_2 = 55$  (Fig. 12).

The autocatalytic nature of the early stages of reaction is clearly evident in Figure 13 [23], which contains a plot of C<sub>2</sub>C<sub>5</sub> olefin selectivity versus contact time at a very low methanol partial pressure. Characteristic sigmoid trajectories are shown by the C<sub>3</sub>C<sub>5</sub> olefins; ethylene increases only slowly. This is consistent with a chain-growth mechanism whereby olefins are homologized by C<sub>1</sub> addition, with ethylene as the "first" olefin.

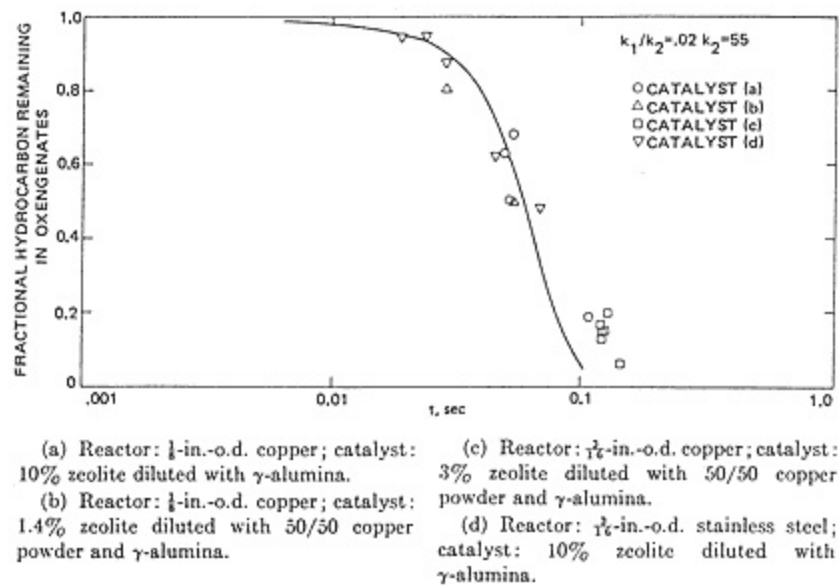


Figure 12  
Autocatalytic kinetic model of Chen and Reagan with experimental data at 370°C, 1 atm.  
(From Ref. 27.)

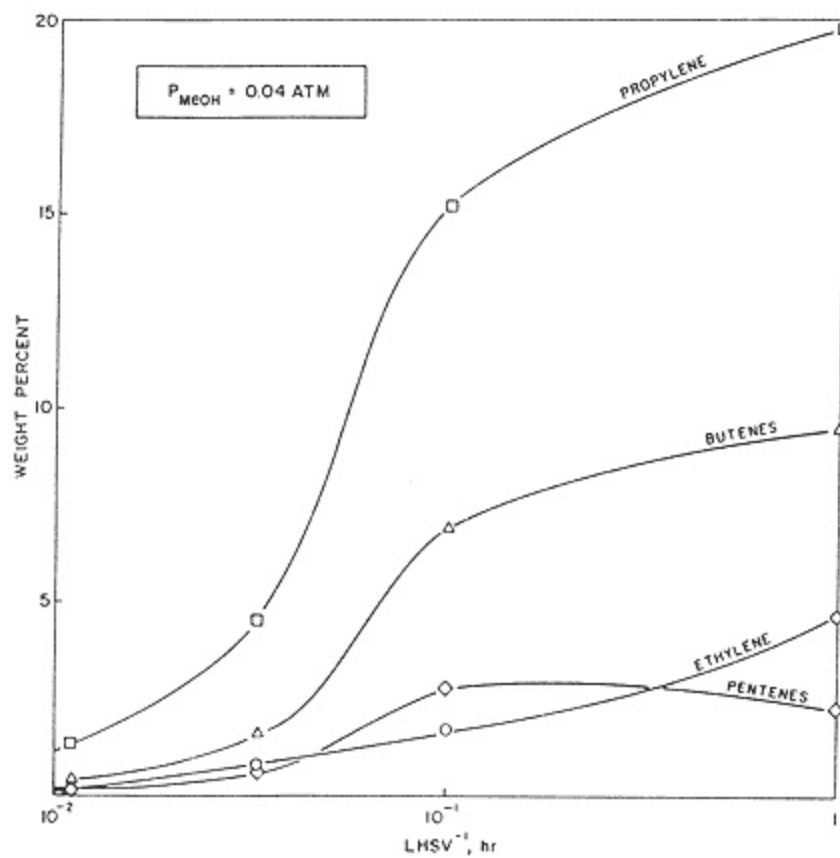


Figure 13

Autocatalysis as evidenced in MTG light olefin selectivity at 370°C, 0.04 atm.  
(From Ref. 23.)

Ono et al. [28,29] modified the model of Chen and Reagan by assuming the first step to be bimolecular:



where A and B are oxygenates and olefins, respectively. With  $x$  = conversion of A and  $w$  = catalyst weight, there results

$$\frac{1}{W} \frac{dx}{dt} = k_2[A]_0(1-x)[(\alpha + \beta) + (1 - \alpha)x] \quad (8)$$

where  $\alpha = k_1/k_2$  and  $\beta = [B]_0/[A]_0$ .

Upon integration, one obtains

$$\ln \frac{\alpha + \beta + (1 - \alpha)x}{(\alpha + \beta)(1 - x)} = k_2 W[A]_0(1 + \beta)t \quad (9)$$

At low initial conversion ( $\beta = 0$ ,  $\alpha \ll 1$ ), Equation (9) reduces to

$$\ln \frac{\alpha + x}{\alpha(1 - x)} = k_2 W(A)_0 t \quad (10)$$

Figure 14 [29] shows the fit to data obtained at three temperatures.

Chang [30] further modified the Chen-Reagan model by including a step representing C-C bond formation via C1 insertion into C-H, initiating auto-catalysis.

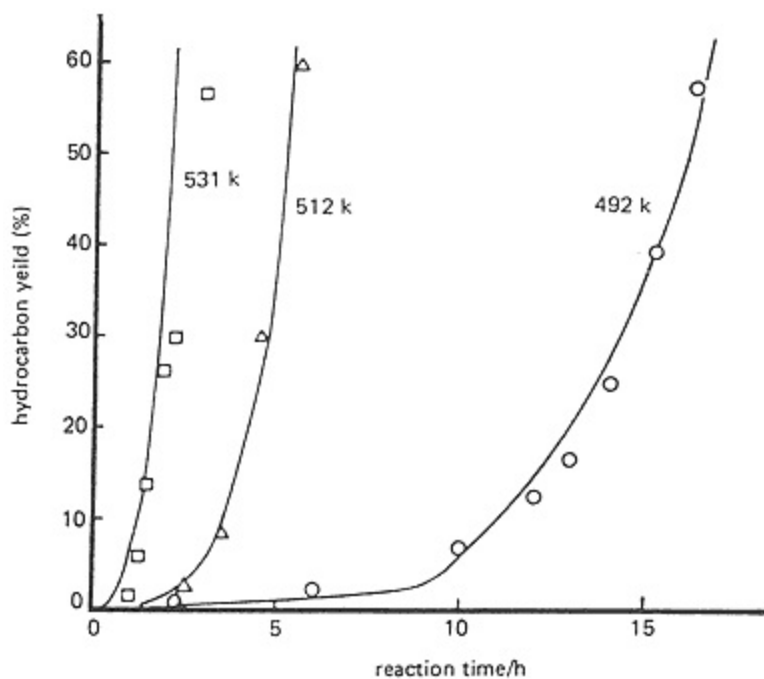


Figure 14  
Autocatalytic kinetic model of Ono et al. (solid lines are calculated).  
(From Ref. 29.)



where A = oxygenate, B = (:CH<sub>2</sub>), C = olefins, and D = paraffins + aromatics.

The carbenelike species B was assumed capable of attacking either oxygenates or olefins. Invoking the steady-state assumption on B and eliminating time, there results

$$-\frac{du}{da} = \frac{1}{A} \left[ \frac{1 + K_1 u}{2 + K_1 u} (1 - K_2 u) + u \right] \quad (12)$$

where  $u = C/A$ ,  $K_1 = k_3/k_2$ , and  $k_2 = k_4/k_1$ .

Equation (12), integrated (with initial conditions  $A = 1$ ,  $u = 0$ ), yields

$$\ln A = \frac{K_1 - 2}{\gamma} \ln \frac{2\alpha u + \beta - \gamma}{2\alpha u + \beta + \gamma} \frac{\beta + \gamma}{\beta - \gamma} - \frac{K_1}{2\alpha} \ln (1 + \beta u + \alpha u^2) \quad (13)$$

where  $\alpha = K_1(1 - K_2)$ ,  $\beta = K_1 K_2 + 2$ , and  $\gamma = \sqrt{\beta^2 - 4\alpha}$ . This was applied to data obtained at three pressures, resulting in the plot in Figure 15.

Anthony [31] and Sedran et al. [32] revised the Chang model to allow net increases in olefin concentration.

A number of MTG kinetic models of increasing complexity have since been proposed [3339].

#### 4.1.7

##### The Mobil MTG Process

Two major versions of the MTG process currently exist. The first, as exemplified by the New Zealand GTG configuration, is a fixed-bed process; the second is a fluidized-bed process. A third process concept, the Topsøe TIGAS [40], integrates methanol synthesis with MTG. This variation uses a multifunctional catalyst for producing a mixed oxygenate feed (including methanol) from synthesis gas and was tested on the pilot plant scale.

##### 4.1.7.1

##### The New Zealand GTG Plant

The fixed-bed MTG was selected for New Zealand as the configuration most readily scaled up. At the time this decision was made, the fluidized-bed version was considered to require more extensive development [22], including devel-

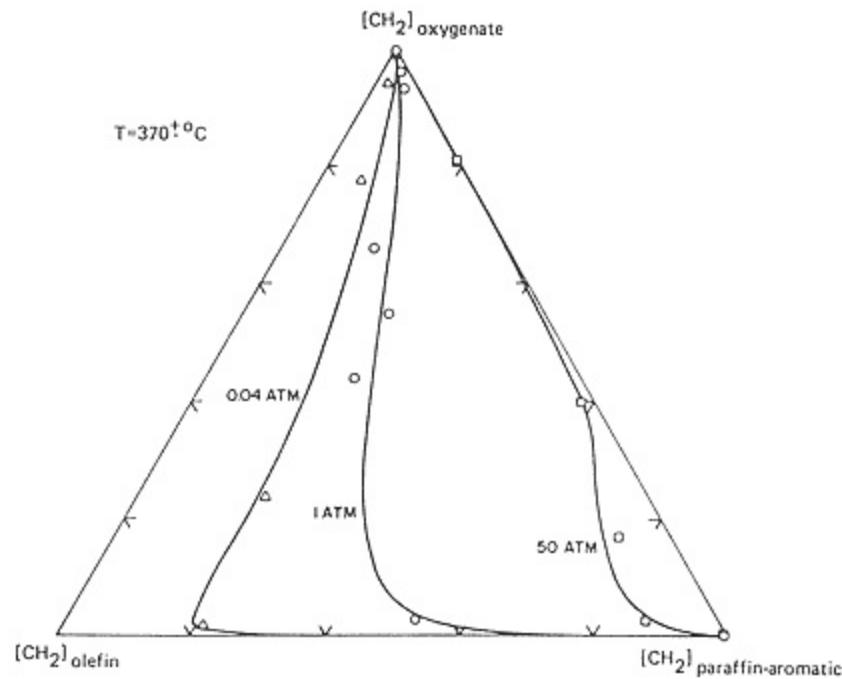


Figure 15  
Kinetic model of Chang (solid lines are calculated).  
(From Ref. 30.)

opment of a fluid catalyst. The New Zealand GTG complex, which was started up in October 1985, is situated on the North Island between the villages of Waitara and Motonui on the Tasman seacoast. A simplified block flow diagram of the complex is shown in Figure 16 [41]. The facility processes over 130 million standard cubic feet per day of natural gas from the offshore Maui gas field, supplemented by gas from the onshore Kapuni field, to methanol and thence to 14,500+ barrels per day of gasoline. Methanol feed to the MTG section is synthesized using the ICI low-pressure process [42] in two trains, each with a capacity of 2200 ton per day. The MTG section itself is single train.

The natural gas feed is desulfurized, combined with medium-pressure steam, and passed through reformer reactor tubes containing a nickel catalyst at 900°C to produce synthesis gas. The synthesis gas, after cooling to 35°C and compression to 1500 psia, is reheated and converted at 250-300°C over the ICI Cu-Zn catalyst to crude methanol (17% water). This is fed directly to the MTG reactor section, where it is converted in two stages to aromatic gasoline.

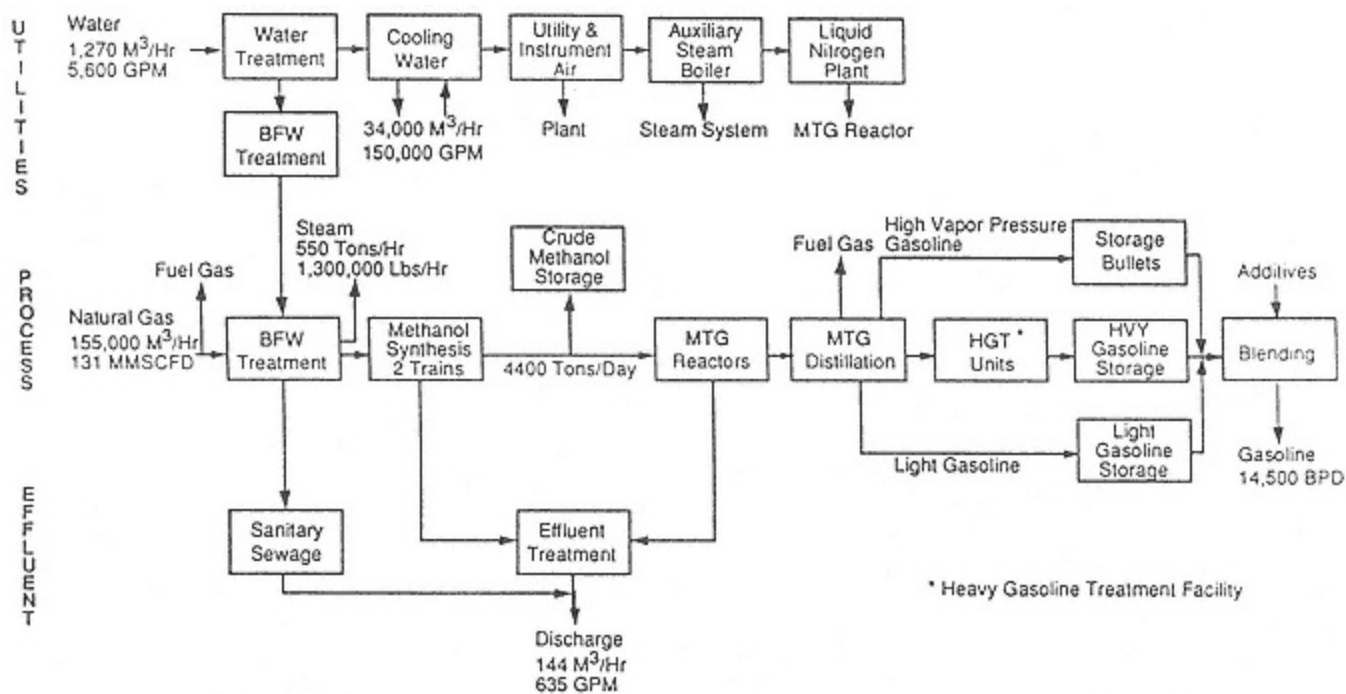


Figure 16  
The New Zealand GTG complex.  
(From Ref. 41.)

A flow diagram of the MTG section is presented in Figure 17 [43]. Methanol feed, vaporized by heat exchange with MTG reactor effluent gases, enters a first-stage dehydration reactor, where an equilibrium mixture of DME, methanol, and water is produced over an alumina catalyst at 300-420°C [43]. Roughly 20% of the reaction heat is removed at this stage. The effluent from the dehydration reactor is combined with recycle gas and enters the conversion reactors containing ZSM-5 catalyst, where it is converted at 360-415°C and 315 psia to the gasoline product. As indicated in the diagram, the second-stage conversion utilizes a system of five fixed-bed swing reactors in parallel. Four of these reactors are on feed while the fifth is in a regeneration mode. The reactors are adiabatic. Heat removal is by means of light gas recycle through the catalyst beds, which limits temperature rise to 420°C at the reactor outlet. After cooling,

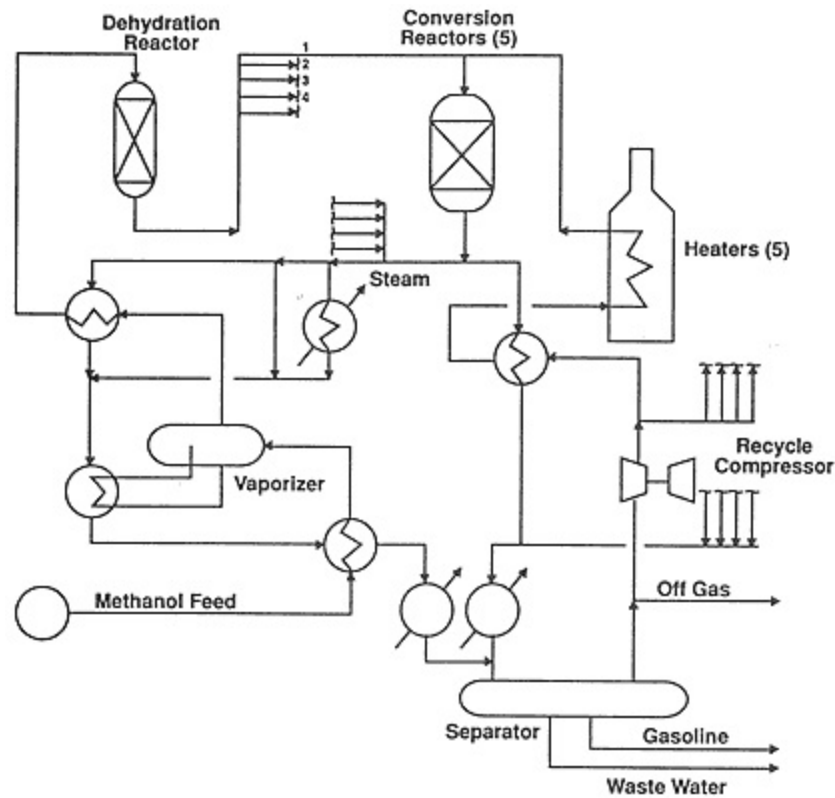


Figure 17  
The MTG section of the New Zealand GTG plant.  
(From Ref. 22.)



condensing, and separation of water, the crude gasoline product is hydrofinished to remove heavy components, mainly durene, and sent to the gasoline pool for blending.

The multiple reactor scheme serves two main purposes: pressure drop minimization and maintenance of constant product composition. As indicated earlier, catalyst aging in fixed-bed MTG occurs through a band-aging mechanism, by which product selectivity changes with increasing catalyst age, becoming more olefinic and less aromatic with stream time. With parallel multiple catalyst beds at different aging states, it is possible to maintain constant overall product selectivity by proper sequencing, or "staggering." Figure 18 [43] provides an example of a reactor operating sequence used to smooth yield variations. Table 3 contains typical gasoline quality data from the New Zealand plant [44]. These results were obtained during January/February 1987 for 97,000 ton gasoline.

The thermal efficiency of a GTG plant depends on the composition of the natural gas as well as the plant design. The MTG reaction per se has high energy efficiency, of the order of 95% based on the lower heating value (LHV), with the remaining 5% of chemical energy released as heat of reaction [25]. The LHV is the appropriate basis since internal-combustion engines do not condense

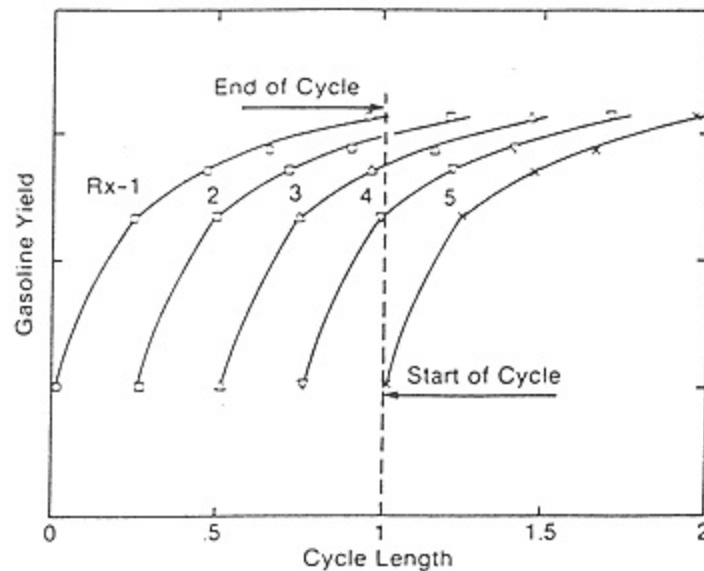


Figure 18  
Typical reactor operating sequence in the New Zealand MTG section.  
(From Ref. 43.)

Table 3 Gasoline Quality, New Zealand GTG Plant

	Average	Range
Density, kg/m <sup>3</sup> at 15°C	730	728733
RVP, psia	12.5	12.113.2
RON	92.2	92.092.5
MON	82.6	82.283.0
Durene content, wt%	2.0	1.742.29
Induction period, min	325	260370
Distillation		
% Evaporated at 70°C	31.5	29.534.5
% Evaporated at 100°C	53.2	51.555.5
% Evaporated at 180°C	94.9	94.096.5
End point, °C	204.5	196209

Source: From Reference 44.

water. The overall thermal efficiency of the New Zealand plant is of the order of 53% [45].

#### 4.1.7.2

##### The Fluidized-Bed MTG Process

Heat management of the highly exothermic MTG reaction is greatly facilitated through use of fluidized-bed reactors. The turbulent bed ensures isothermality through the reaction zone and, owing to its excellent heat-transfer properties, enables steam generation by direct exchange with steam coils in the bed. Furthermore, a fluidized-bed system with continuous catalyst withdrawal, regeneration, and recycle can maintain constant catalyst activity and therefore does not require the use of multiple reactors.

Although not as yet commercialized, the fluidized-bed MTG process has been scaled up [22,25,46,47] and demonstrated on a semiworks scale of 100 barrels per day [48,49]. A simplified flow diagram of the 100 bpd demonstration unit appears in Figure 19 [25]. As depicted, the reactor system consists of three principal parts: the reactor, the catalyst regenerator, and an external catalyst cooler. The reactor was also equipped with internal heat-exchanger tubes in the catalyst bed to allow evaluation of that option for heat removal.

Feed to the reactor is a simulated crude methanol stream consisting of a mixture of 83% methanol and 17% water. The reactor accommodates a dense fluid catalyst bed measuring 2 ft in diameter by 40 ft in height. The feed can either be injected as a liquid or vaporized and superheated before entering the reactor. The feed passes through the bed, where it is converted quantitatively

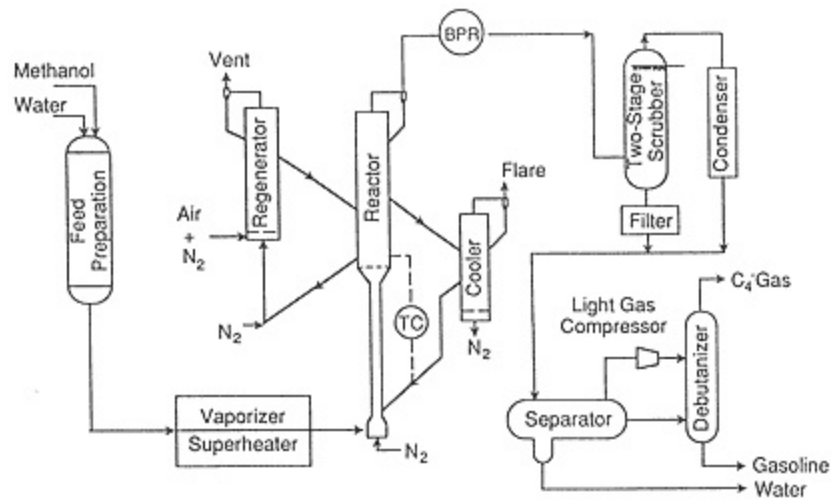


Figure 19  
Flow diagram of the 100 bpd fluidized-bed MTG demonstration unit.  
(From. Ref. 25.)

to hydrocarbons and water in a single pass. Reaction conditions are 4060 psia and 380-430°C, with methanol feed rate of 500-1050 kg/h. After catalyst disengagement, product vapor is condensed, the condensate collected in the separator, and the hydrocarbon layer drawn off. The hydrocarbon product is sent to the debutanizer column, where it is split into  $C_4^-$  and  $C_4^+$  fractions.

The 100 bpd fluidized-bed plant was installed in Wesseling, Germany and began MTG operations in December 1982. The plant logged 8600 h on-stream, processing a total of 6870 ton methanol to gasoline.

#### 4.1.7.3 Fixed-Bed and Fluidized-Bed MTG Compared

The advantages in fluidized-bed operation for heat management and for maintenance of constant catalyst activity have already been noted. Other advantages include higher yield, quality, lower durene, and potentially lower investment costs. The fluidized-bed operation requires catalysts with low attrition properties. In the design of a fluidized-bed reactor system, particular attention must be given to the reactor fluid dynamics to ensure complete methanol conversion. This is critical to avoid the need for additional distillation facilities to recover unreacted feed.

Typical process conditions and product yields from fixed- and fluidized-bed MTG are compared in Table 4 [22]. The fluidized-bed hydrocarbons are seen to be more olefinic than the fixed bed. In the fixed-bed process, the recycle of

Table 4 Comparison of Fixed- and Fluidized-Bed MTG Process Conditions and Product Yield

	Fixed bed	Fluidized bed
Conditions		
Methanol/water charge (wt/wt)	83/17	83/17
Dehydration reactor inlet temperature, °C	316	
Dehydration reactor outlet temperature, °C	404	
Conversion reactor inlet temperature, °C	360	413
Conversion reactor outlet temperature, °C	415	413
Pressure, kPa	2170	275
Recycle ratio, mol/mol charge	9	1
Yields, wt% of methanol charged		
Methanol + ether	0.0	0.2
Hydrocarbons	43.4	43.5
Water	56.0	56.0
CO, CO <sub>2</sub>	0.4	0.2
Gasoline (including alkylate), RVP 62 kPa (9 psi)	85.0	88.0
LPG	13.6	6.4
Fuel gas	1.4	5.6
Total	100.0	100.0
Gasoline octane (R + 0)	93	97

Source: From Reference 50.

light gas, in addition to removing heat, serves to reinsert the constituent olefins into the reaction path, enhancing their conversion as well as increasing reaction rate by their interaction with the methanol-DME feed (autocatalysis). In contrast, the fluidized-bed operates in a single-pass mode. By "fine-tuning" catalyst activity through adjustment of catalyst recirculation rate, the product propylene and butenes are readily brought into balance with the isobutane, thereby allowing supplemental downstream alkylate synthesis to increase yield and quality of the finished gasoline.

#### 4.1.8

##### MTG Economics

As stated at the beginning of the chapter, the MTG process was developed in response to the 1973 oil shock and the rapid rise in oil prices. These prices reached a peak of nearly \$40/bbl in 1980. However, prices were not to remain at that high level for long, because of a combination of factors, including conservation measures, reduced demand, and the inability of the Organization of Petroleum Exporting Countries to agree on production levels. Crude prices began

to decline soon after, dipping briefly to below \$10/bbl in 1986. With the exception of a single upward spike as a result of the 19891990 Gulf War, crude prices have stabilized as of this writing to \$1520/bbl. At these prices MTG is not competitive with petroleum for gasoline production, although there may exist unique situations involving remote natural gas for which MTG might be considered today. Economics for a New Zealand type of plant based on the U.S. Gulf Coast are summarized in Table 5 [50]. Although these data are taken from an earlier analysis assuming a 1987 start-up, it is unlikely that the conclusions would change significantly even with present advances in methanol technology, because the process is highly capital intensive and capital recovery will remain the dominant factor. Nevertheless, since synthesis gas can be produced from any gasifiable carbonaceous material, including coal and biomass, such processes as the MTG may assume increasing importance as sources of oil and natural gas are depleted in the future.

#### 4.2 Conversion of Methanol to Olefins

Light olefins are intermediates in the MTG reaction, according to Equation (3). By proper selection of reaction conditions and with suitable catalyst design, it is possible to decouple the "olefination" step from aromatization. This is the basis of the Mobil MTO process, which utilizes fluidized-bed technology. The process has not yet seen commercialization, but has been scaled up [51,52] and demonstrated on a 100 bpd scale. Alternatively, olefin yield can be increased by operating under partial conversion conditions, recovering the intermediate

Table 5 GTG Plant Economicsa

Natural gas, bcf/year	44
Methanol, t/sd	4,400
Gasoline, bpsd	14,600
Inventment, MM\$b	895
Gasoline cost, cents/gal	
Natural Gas at \$1.00/MMBtu	22
Operating	34
Capital at 12% DCF RORc	82
Total	138

a Bases: New Zealand type plant, 1982 technology, U.S. Gulf Coast, 1987 start-up, equity financing.  
b Not included are land, pipeline, and venture costs. Debt financing: ~ 60 cents/gal; total = 116 cents/gal. DCF, ROR,  
Source: From Reference 50.

olefins, and recycling unreacted feed. This approach was adopted in part for MTC (methanol-to-chemicals) [53], an ethylene-selective MTO process developed by AECI of South Africa [54]. This process, utilizing coal-derived methanol, has not been commercialized.

#### 4.2.1

##### Catalysts for the MTO Reaction

Not surprisingly, ZSM-5 is an effective MTO catalyst and has been subject of very intensive scrutiny. Among the host of other catalysts [55,56] reported in the literature to be active for MTO, the silicoaluminophosphate molecular sieves SAPO-17 and SAPO-34 [57,60] seem noteworthy. The framework structures of SAPO-17 and -34 are topologically related to the zeolites erionite and chabazite, respectively [57,58]. These zeolites have eight-ring pore openings, and hence their SAPO analogs should produce aliphatics to the exclusion of aromatics. This has been verified experimentally [59]. Representative MTO selectivity data for ZSM-5 and SAPO-34 are shown in Tables 6 [24] and 7 [59]. SAPO-34 is apparently effective at lower temperatures than ZSM-5 for MTO; however, data on the long-term thermal and steam stability and regenerability of the SAPO have not been published.

#### 4.2.2

##### Kinetic Parameters

The discussion of MTG kinetic effects just presented is generally applicable to MTO. Olefin selectivity is improved by decreasing methanol partial pressure, increasing temperature, and increasing zeolite  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . An additional effect, that of varying zeolite crystallite size, was reported by Howden et al. [61], who found that when the crystallite size was reduced from 30 to 3  $\mu\text{m}$ , ethylene selectivity increased. This was attributed to enhanced diffusivity of light products, which reduces their opportunity for further reaction.

The effect of increasing ZSM-5  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is demonstrated in Figure 20 [24], where  $\text{C}_2\text{C}_5$  olefin selectivity is plotted against contact time at 500°C and 1 atm. In addition to the selectivity increase with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , each reaction trajectory passes through an expected maximum, which shifts to the right (higher contact time) with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$ .

In principle, the kinetic models developed for MTG should be applicable to MTO. However, under conditions in which olefination is largely decoupled from aromatization, a simple reaction scheme



where A = oxygenates (as  $\text{CH}_2$ ), B = olefins, and C = aromatics + paraffins,

Table 6 Methanol Conversion to Olefins over ZSM-5

Catalyst SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	70	142	500	1670
LHSV, h <sup>-1</sup>	100	50	14.4	10
Total product distribution, wt%				
H <sub>2</sub> O	55.93	55.96	51.77	54.00
DME	0.20	0.98	3.67	0.59
MeOH	0.29	2.50	2.90	0.95
CO	0.09	0.05	0.10	0.84
CO <sub>2</sub>	0.01	0.01	0.04	0.59
H <sub>2</sub>	0.01	0.02	0.15	0.42
Hydrocarbon	43.47	40.48	43.37	42.53
% Conversion	99.43	96.14	92.00	98.23
Hydrocarbon distribution, wt%				
Methane	0.99	1.26	1.15	3.67
Ethane	0.12	0.13	0.11	0.23
Ethylene	10.48	9.94	7.43	7.75
Propane	3.76	1.92	0.56	0.48
Propylene	22.60	35.14	39.40	37.59
i-Butane	7.82	4.32	0.73	0.60
n-Butane	1.60	0.74	0.21	0.16
Butanes	16.56	17.61	21.58	20.43
i-Pentane	4.80	2.97	0.81	0.62
n-Pentane	0.65	0.52	0.52	0.47
Pentenenes	5.91	8.35	12.13	10.25
C <sub>6</sub> <sup>+</sup> nonaromatic	10.63	9.50	7.59	8.98
Benzene	0.22	0.12	0.17	0.18
Toluene	1.28	0.67	0.70	0.51
Ethylbenzene	0.32	0.18	0.16	0.16
Xylenes	6.87	3.58	3.71	2.80
Ag	4.31	2.55	2.61	3.98
A <sub>10</sub> <sup>+</sup>	1.90	0.47	0.40	1.48
C <sub>1</sub> C <sub>5</sub>	19.74	11.88	4.10	6.24
C <sub>2</sub> -C <sub>5</sub> <sup>2+</sup>	55.55	71.04	80.55	76.03
C <sub>6</sub> <sup>+</sup> PON	10.63	9.50	7.59	8.98
Aromatics	14.08	7.58	7.77	8.72

Source: From Reference 24.

was found to be adequate and instructive [24]. Assuming the disappearance of oxygenates and olefins to be pseudo-first order, the parameters  $k_1$  and  $k_2$  can be determined in a straightforward manner. Figure 21 is a first-order plot of the

Table 7 Methanol Conversion to Olefins over SAPO-34a

	375°Cc	Molar selectivity (%)b		
		400°Cc	425°Cc	450°Cd
Ethylene	43.0	46.7	51.4	61.1
Ethane	0.8	0.6	0.6	0.7
Propylene	41.8	36.7	32.5	27.4
Propane	0.5	0.5	0.5	Trace
Butenes	10.8	11.9	9.3	5.4
C5	1.7	1.6	1.4	0.6
C6	Trace	Trace	Trace	Trace
Methane	1.3	2.0	4.3	4.8
Dimethyl ether	Trace			
C2C4 olefin efficiency	95.6	95.3	93.2	93.9
Ethylene-propylene	1.03	1.27	1.58	2.23
Run time, h	5.2	6.3	6.2	11.0
Methanol	100	100	100	100
Conversione	0.9	1.5	5.5	1.0
Carbon dioxide efficiency, %e	0.9	1.5	5.5	1.0

a WHSV (methanol): 0.830.87 h<sup>-1</sup>, WHSV (water): 1.952.04 h<sup>-1</sup>.

b To carbon-containing products exclusive of carbon dioxide or involatile deposits, such as coke, on catalyst.

c SAPO-34 (A) (Si<sub>0.07</sub>Al<sub>0.51</sub>P<sub>0.42</sub>)O<sub>2</sub>.

d SAPO-34 (B), prepared identically to A: not analyzed.

e Molar, based on all volatile carbon-containing products.

Source: From Reference 59.

disappearance of oxygenates at 400, 450, and 500°C and 1 atm. The HZSM-5 catalyst in this example had SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 500. The parameter k<sub>2</sub> can then be estimated [62] from

$$[B] = \frac{k_1}{k_2 - k_1} (e^{-k_1 \tau} - e^{-k_2 \tau}) \quad (15)$$

In Figure 22 experimental data are fit using the model. The data in Figure 22AC were obtained at 400/500°C and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 500, and in Figure 22D, at 500°C and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 400. The small deviations at low conversion are attributed to autocatalysis, which was not taken into account in the simple model. The plot in Figure 23A shows the increase in the ratio k<sub>1</sub>/k<sub>2</sub> with increasing temperature and is the physical basis for decoupling of the two reactions, that



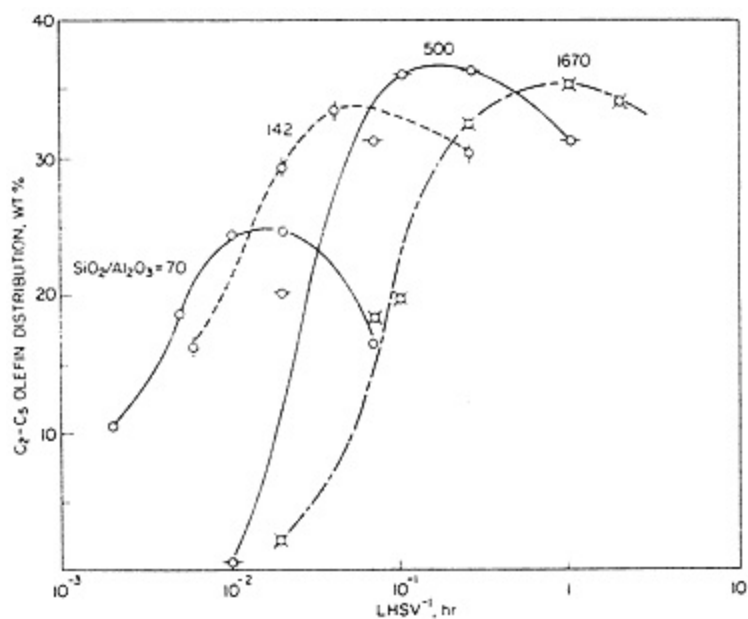


Figure 20  
Light olefin selectivity as a function of ZSM-5 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> at 500°C, 1 atm.  
(From Ref. 28).

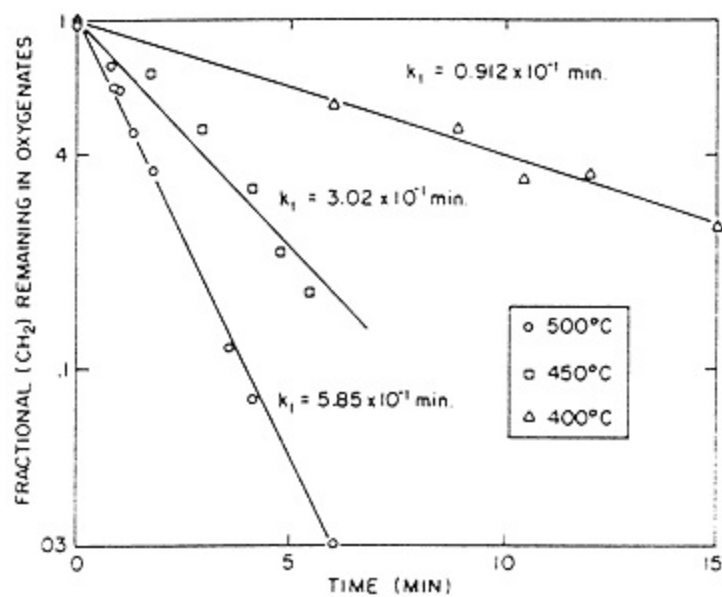


Figure 21  
First-order plot of oxygenate disappearance in MTO.  
(From Ref. 24.)

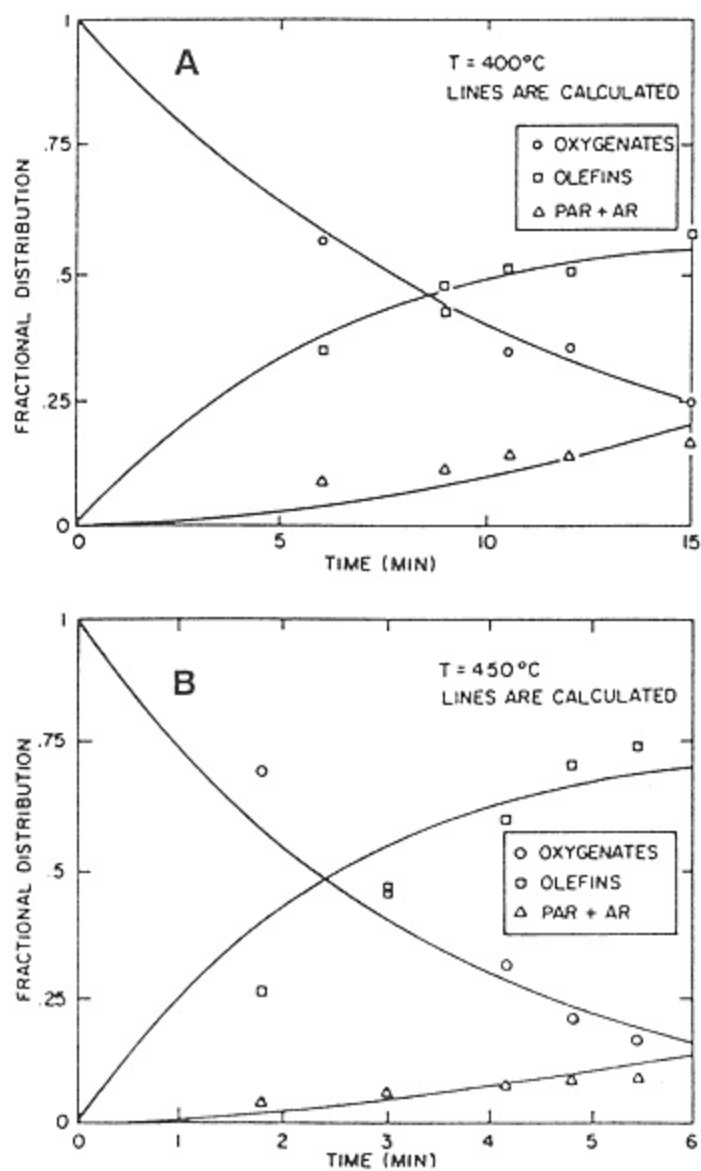
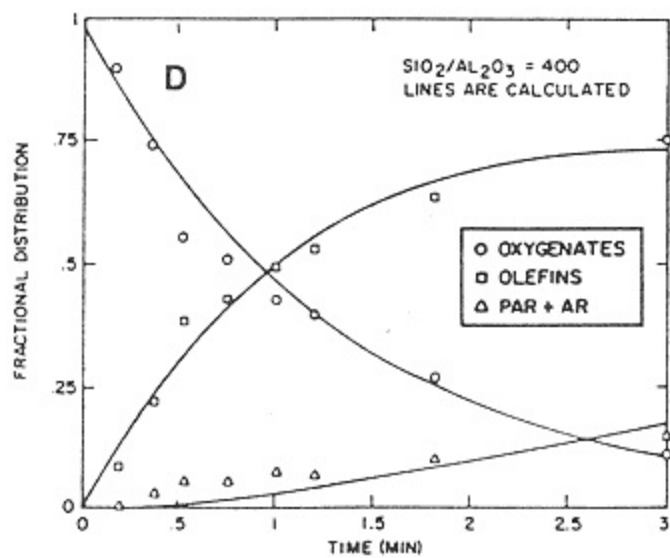
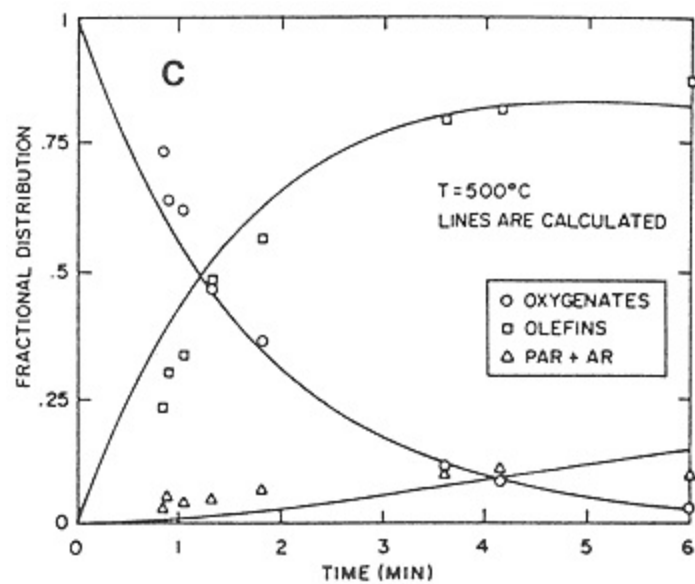


Figure 22  
MTO data fitted to simple  $A \rightarrow B \rightarrow C$  kinetics  
(From Ref. 24.)



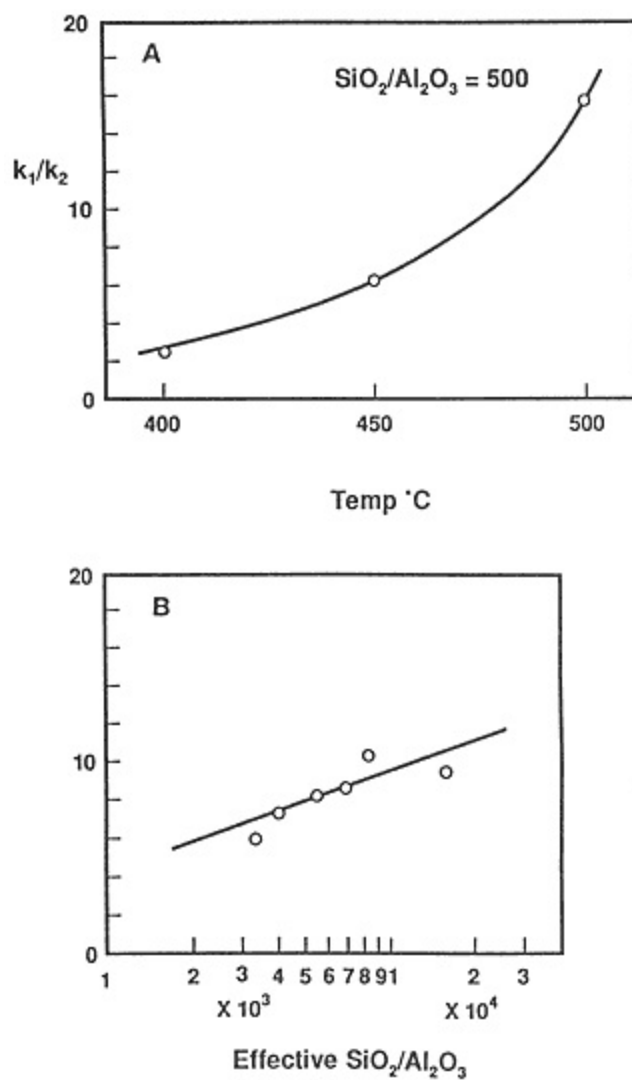


Figure 23  
Variation in  $k_1/k_2$  with temperature and catalyst  $\text{SiO}_2/\text{Al}_2\text{O}_3$ .

is, a difference in apparent activation energy. A plot of  $k_1/k_2$  versus catalyst  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is presented in Figure 23B, showing a similar effect of catalyst activity on the relative rates of the two reactions.

#### 4.2.3

#### The Mobil MTO Process

Large-scale demonstration of the MTO process was carried out in same 100 bpd unit used for the MTG fluidized-bed demonstration (Fig. 19). Process conditions were 3252 psia, 470–515°C, and methanol feed rate of 570–620 kg/h. Catalyst makeup rate was less than 0.5% of inventory per day. The demonstration unit accumulated 3600 h on-stream and processed 2130 ton methanol. Methanol conversion was 99.9+% throughout the run. Typical product distribution is shown in Figure 24 [49], which plots hydrocarbon yield versus propane to propene ratio, a reaction index that is a measure of severity. Higher olefins yields are reflected in lower values of the reaction index. The unit achieved a maximum of 60% olefin yield during the demonstration. Operation at lower pressure or with diluents, both known to increase olefin yield, was not implemented during this run.

A potential application of MTO olefins that has received considerable attention is their conversion to distillates and/or gasoline via the Mobil MOGD process [6365]. Typical MOGD process yields with  $\text{C}_3\text{C}_6$  olefin feed are presented in Table 8 [52]. With the MOGD process, the flexibility of MTG/MTO technology may be significantly enhanced, as seen in Figure 25 [52].

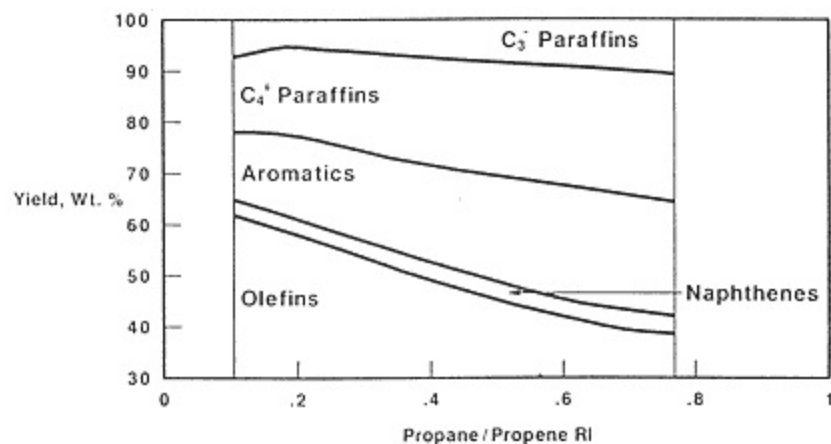


Figure 24  
Light olefin distribution in MTO as a function of the propane-propylene reaction index.  
(From Ref. 49.)

Table 8 Typical MOGD Yields from C3C6 Olefins

	Maximum distillate mode	Gasoline mode
C1C3	1	4
C4	2	5
C5165°C gasoline	15	
165°C + distillate	82	
C5200°C gasoline		84
200°C + distillate		7

Source: From Reference 52.

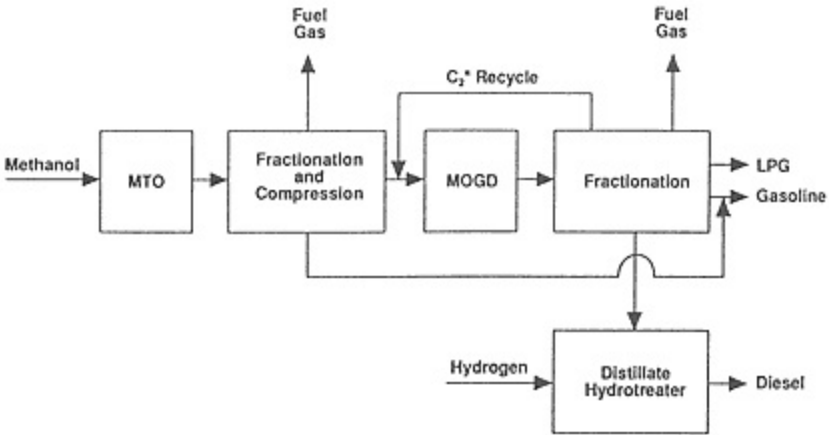


Figure 25  
Gasoline and distillate synthesis from methanol with MTO and MOGD.  
(From Ref. 52.)

#### 4.2.4 The MTC Process

The MTC process was designed to maximize ethylene and propylene from coalbased methanol by MTO. This is achieved by addition of excess steam during

the reaction. This reduces methanol partial pressure, which was shown previously to increase olefin selectivity. Excess steam provides an additional benefit, not well understood, of increasing ethylene selectivity over other olefins under MTO conditions [53,66]. Representative data obtained using a small fluidized-bed reactor is shown in Table 9 [53].

A simplified block diagram of the MTC process appears in Figure 26 [54]. The general layout is quite similar to that of the New Zealand plant MTG section. Fresh methanol and makeup water, along with recycle methanol-DME, is vaporized, combined with recycle steam, and fed to the DME reactor, where a mixture of methanol, DME, and water is produced. The DME reactor effluent then passes through a series of conversion reactors, where the main reactions occur. No design information on the conversion section has been published to date. After cooling, separation, and fractionation, a hydrocarbon product consisting of 30% ethylene, 20% propylene, 12% methane and ethane, 13.14% liquid propane gas (LPG), and 35% gasoline is recovered. The MTC pilot plant was designed to process 12 ton per day of methanol.

Conditions	Feed methanol/water (wt/wt)		
	83/17		16/84
Temperature, °C	299	343	324
Methanol partial pressure, kPa	105	105	28
Methanol WHSV	0.4	0.4	0.2
Oxygenate conversion, %	52	84	62
Hydrocarbon product, wt%			
Ethylene	21.3	18.8	27.6
Propylene	17.2	11.7	17.5
Butenes	7.1	6.5	6.1
Pentenes	2.1	2.9	1.3
C1C5 paraffins	18.3	20.8	24.7
C <sub>6</sub> <sup>+</sup> paraffins and olefins	19.5	23.0	16.2
Aromatics	14.5	16.3	6.6
Total	100.0	100.0	100.0

Source: From Reference 53.

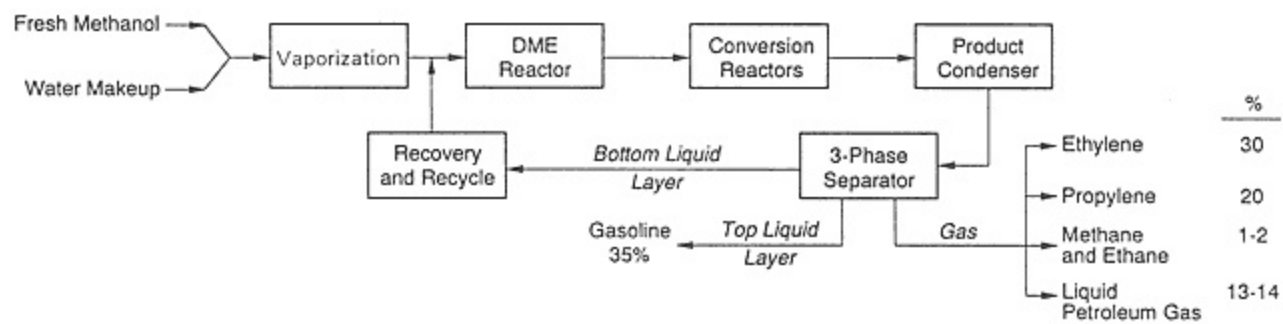


Figure 26  
Simplified AECI ethylene-selective MTO process.  
(From Ref. 54.)



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## 5 Methanol to Chemicals

Harold H. Kung  
Northwestern University, Evanston, Illinois

Kevin J. Smith  
University of British Columbia, Vancouver, British Columbia, Canada

### 5.1 Acetic Acid

In 1992, about 6.5 billion lb acetic acid was produced worldwide, of which about 3.6 billion lb was produced in the United States [1]. The current commercial processes for its production include oxidation of ethanol (acetaldehyde), oxidation of butane-butene mixture or naphtha, and carbonylation of methanol or methyl acetate. These are catalytic processes. The last, liquid-phase carbonylation of methanol using a rhodium and iodide catalyst, has become the dominant process since its introduction in the late 1960s, and accounted for about half the production of acetic acid in the United States [2]. That represents a conversion of  $1.5 \times 10^6$  ton per year of methanol into  $2.8 \times 10^6$  ton per year of acetic acid. In the United States, 80% of actual plant operation capacity is based on this technology [3]. The reaction is thermodynamically favorable [4], and the theoretical conversion is practically 100% at 389 K:



where  $\Delta G_{389\text{K}} = 72.79 \text{ kJ/mol}$  and  $\Delta H_{389\text{K}} = 133.82 \text{ kJ/mol}$ .

The reaction of carbonylation of methanol was described by Badische Anilinund-Soda-Fabrik (BASF) as early as 1913. In 1963, BASF began large-scale production of acetic acid by this reaction using a cobalt carbonyl catalyst with

an iodine compound as a cocatalyst [5,6]. The catalytically active agents are  $\text{Co}_2(\text{CO})_8$  and HI, which can be produced in situ using cobaltous iodide. The process must be operated under rather severe conditions to obtain commercially attractive yields: 70 MPa pressure (700 atm) and 250°C. The high pressure and the corrosive nature of iodine resulted in rather high equipment and operation costs.

### 5.1.1 Low-Pressure Methanol Carbonylation (Monsanto) Process

In 1968, a new methanol carbonylation process was disclosed by Monsanto, using a much more active catalyst of rhodium salt and iodide cocatalyst than the cobalt-iodide system [79]. The reaction temperature is about 180°C, and the process pressure is reduced to 3.34.4 MPa (3040 atm). The catalyst is highly selective, producing acetic acid or its methyl ester with greater than 99% yield based on methanol and at least 90% based on carbon monoxide [6]. In a laboratory test, the selectivity for such by-products as ethanol, ethanal (acetaldehyde), propanoic acid, propanal (propionaldehyde), butanal (butyraldehyde), and butanol can be as low as 0.1% in the liquid. There are negligible amounts of hydrogen, carbon dioxide, and methane in the gas phase if CO is used as the feed [8]. Since its introduction, the Monsanto process has been used in all new plants because of the lower operating and capital costs as a result of the less stringent process conditions.

The Monsanto process and the higher pressure BASF processes have been reviewed [3,1012]. In the Monsanto process (Fig. 1) [9], methanol and carbon monoxide are fed to a continuous reactor system. The corrosive nature of iodine in an acid medium requires the use of a highly corrosion-resistant metal reactor (made of such material as Hastelloy C). The acetic acid produced is purified by conventional distillation. The purified acetic acid is sent to a drying column. The dried acetic acid is removed as the bottom product and sent to the product column to reduce the small concentration of propanoic acid. The typical composition of the acetic acid from this process is [9] as follows:

Acetic acid, 99.9 wt%  
 Water, 0.03 wt%  
 Formic acid, < 0.03 wt%  
 Acetaldehyde, 0.004 wt%  
 Propionic acid, < 40 ppm  
 Chloride, < 1 ppm  
 Iron, < 1 ppm

Because of the low operating temperature, only a part of the heat of reaction (which is relative small) is recovered to preheat the feed gas.

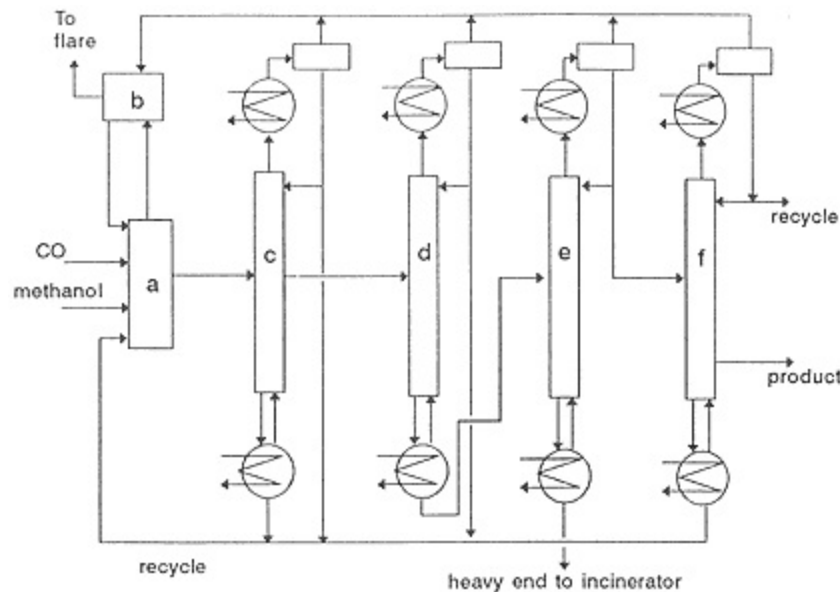


Figure 1

The Monsanto process for methanol carbonylation to acetic acid:

(a) reactor; (b) scrubber system; (c) light-end column; (d) drying column;  
(e) product column; and (f) finishing column.

[Adapted from H. D. Grove, *Hydrocarbon Proc.*, November:76 (1972).]

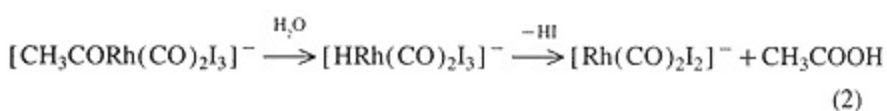
## 5.1.2

### Catalyst and Reaction Mechanism

A wide variety of rhodium compounds can be used as the catalyst precursor [8,11]. They include  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ ,  $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ ,  $\text{RhCl}(\text{PPh}_3)_3$ ,  $\text{Rh}(\text{CO})_2(\text{AsPh}_3)\text{I}_2$ , and  $[\text{Rh}(1,5\text{-cyclooctadiene})\text{X}]_2$ , with  $\text{X} = \text{Cl}, \text{I}, \text{OMe}, \text{OAc}, \text{OPh}$ , and other complexes. The observed reaction rates using different rhodium compounds are essentially the same, although the duration of the induction period may vary. Iridium compounds are also effective catalysts, but none has been commercialized. The reaction kinetics indicates that the reaction mechanism for the iridium catalyst is more complex than for the rhodium catalyst, but the gross behavior is similar. Various iodide promoter compounds are equally effective, such as aqueous hydrogen iodide, methyl iodide, calcium iodide, and iodine. Alkali iodide salts, such as sodium iodide, are less effective, however, although lithium iodide has been claimed to be an exception [10c]. Bromides are also less effective than iodides [13].



That similar activities and product selectivities are obtained with different rhodium compounds as catalyst and iodine compounds as cocatalyst suggests that the different compounds eventually are converted to the same active catalytic species under reaction conditions [8,13,14]. Indeed, the working catalyst has been identified as  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  (species 1 in Fig. 2). Most of the iodine exists as methyl iodide under reaction conditions, and the portion that exits the reactor should be recovered and recycled. The catalytic cycle is shown in Figure 2. The oxidative addition of methyl iodide to  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  to form the methylrhodium complex 2 is believed to be the rate-limiting step. The resulting complex is unstable and rapidly isomerizes by methyl migration of an acetyl monocarbonyl complex 3 [8]. Addition of CO to this complex 3 results in a labile six-coordinated acetyl complex 4. In the reaction mixture containing water and methanol, 4 may react with water, yielding acetic acid directly [Equation (2)], or undergo partial hydrolysis or methanolysis to yield acetic anhydride or methyl acetate [12].



Under the conditions of industrial operation, the rate of methanol carbonylation reaction has been found to be zeroth order in the partial pressure

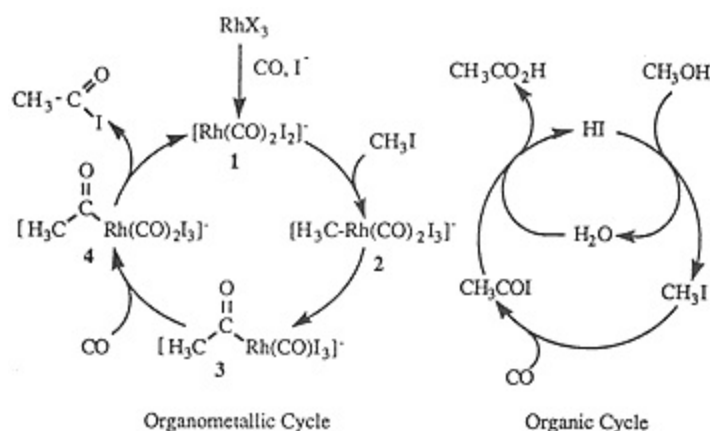


Figure 2

Catalytic cycle involved in methanol carbonylation to acetic acid.  
(Reprinted with permission from G. Parshall and S. Ittel, *Homogeneous Catalysis: The Applications and Chemistry of Catalysis*, 2nd ed., copyright © John Wiley and Sons, New York, 1991.)

of carbon monoxide and zeroth order in the concentration of methanol (i.e., the rate is independent of these concentrations). However, it is first order in the concentrations of rhodium and iodide (i.e., the rate is directly proportional to these concentrations). It is not affected by the presence of hydrogen. In fact, the presence of hydrogen has no effect on the product distribution either [8]. The dependence of the rate on the concentrations of the reactants and catalysts is quite different for the cobalt-catalyzed carbonylation reaction.

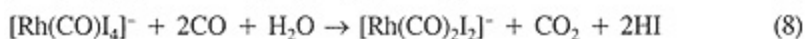
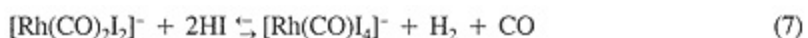
In the reaction mixture, several chemical equilibria are established rapidly:



The rapid equilibrium ensures that all the methanol charged into the reactor is ultimately converted to acetic acid. The equilibrium constant for Equation (5) strongly favors methyl iodide and water. This ensures a supply of methyl iodide for addition to  $[\text{Rh}(\text{CO})_2\text{I}_2]$ . It also plays an important role in limiting the rate of water-gas shift reaction [Eq. (6)], which is the source of loss of carbon monoxide:



The water-gas shift reaction is catalyzed by  $[\text{Rh}(\text{CO})_2\text{I}_2]$ . The proposed reaction cycle is [13,14]:



Equation (8) is presumably the rate-limiting step. Its rate depends on the concentration of  $[\text{Rh}(\text{CO})\text{I}_4]^-$ , which in turn depends on the concentrations of  $[\text{Rh}(\text{CO})_2\text{I}_2]$  and HI. Thus the equilibrium established by Equation (5), which limits the concentration of HI, controls the extent of the water-gas reaction. That alkali halides are less effective cocatalysts than other iodides may be because they do not regenerate methyl iodide rapidly.

As mentioned earlier, a number of iridium compounds have been shown to be effective catalysts for the methanol carbonylation reaction [11,13]. Nickel catalysts have also been found to be effective, particularly when used with compounds of Sn, Cr, Mo, or W [10c,15]. Heterogenized rhodium catalysts, prepared by supporting rhodium compounds on a solid or by anchoring a rhodium complex to a polymer matrix, are also catalysts. However, none of these have been commercialized. In the latter case, the slow dissolution of rhodium is a major problem.

### 5.1.3

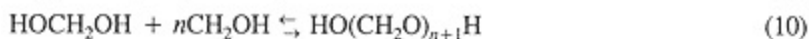
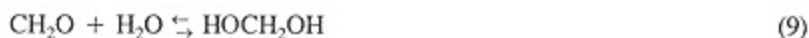
#### Future Prospects

The methanol carbonylation process can be integrated quite naturally into a large-scale methanol plant [9]. The reactant CO can be obtained readily by separation from the synthesis gas used in methanol synthesis. With the large proven reserve of natural gas in the world, this process is in a very secure position compared with the hydrocarbon-based processes. It is also easily adaptable to the use of coal as a source of raw material, since there are proven economic routes to produce synthesis gas from coal.

## 5.2

### Formaldehyde

In 1991, the U.S. annual rate of production of formaldehyde was 7.0 billion lb [1]. Formaldehyde is usually available commercially as an aqueous solution. Aqueous solutions containing 30 wt% formaldehyde are stable at room temperature, but solutions containing higher concentrations become cloudy on storage because of the formation of poly(oxymethylene)glycol [Eqs. (9) and (10)]. Technical-grade formaldehyde solutions contain a small amount of methanol, which suppresses the polymerization process.



Industrial production of formaldehyde is by catalytic oxidation of methanol using either a silver or an iron-molybdenum mixed-oxide catalyst. The two processes differ in the temperature of operation and the methanol-air ratio in the feed, the process using silver catalyst being at a higher temperature of 600–700 versus 270–350°C in the other process and employing a methanol-air ratio less than stoichiometric versus excess air.

Formaldehyde can be formed from methanol by oxidative [Eq. (11)] or nonoxidative dehydrogenation [Eq. (12)]. Table 1 shows the thermodynamic data for these two reactions. For the lower temperature mixed-oxide-catalyzed process, the oxidative pathway is the only thermodynamically favorable reaction. However, for the higher temperature silver-catalyzed process, the nonoxidative process also becomes thermodynamically favorable. Thus both nonoxidative and oxidative pathways contribute in this process.



Table 1 Enthalpy and Gibbs Free Energy Changes of Oxidative and Nonoxidative Dehydrogenation of Methanol

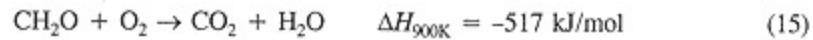
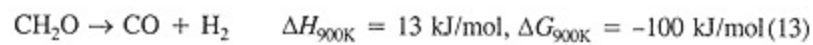
Reaction	kJ/mol	Temperature (°K)					
		400	500	600	700	800	900
$\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$	$\Delta G$	41	29	17	5	7	20
	$\Delta H$	87	89	90	91	92	92
$\text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$	$\Delta G$	183	190	197	204	211	218
	$\Delta H$	137	130	124	118	112	106

Source: Thermodynamic data from I. Barin, Thermochemical Data of Pure Substances, VCH, Weinheim, 1989.

## 5.2.1

### Silver-Catalyzed Process

This process is typically operated at 600–700°C (873–973 K) using a methanol-air ratio that is higher than stoichiometric (stoichiometric ratio 0.4) and outside the upper flammability limit (36.5 vol% of methanol in air). In this range of temperature, both the oxidative [Eq. (11)] and the nonoxidative [Eq. (12)] dehydrogenation process are operative. The carbon-containing by-products are primarily carbon oxides formed by the following reactions:



The contribution from the oxidative and the nonoxidative pathway to the production of formaldehyde depends on the catalyst used and the process conditions. The amounts of process air (i.e., methanol-air ratio) and inert diluents control the extent of the exothermic oxidation reactions (11), (14), and (15), which in turn control the reaction temperature that determines the extent of the endothermic reactions (12) and (13). Water and recycled inert gas that contains nitrogen and carbon dioxide are used as diluents.

The silver-catalyzed process can be operated in the mode of either complete or incomplete conversion of methanol [17]. In the complete conversion mode, the methanol conversion is 97–98%. In the incomplete conversion mode, it is 77–87%. A schematic for the silver-catalyzed process is shown in Figure 3. The two modes of operation share many features. The major difference between them is the need to separate the unreacted methanol present in the incomplete conversion mode by distillation.

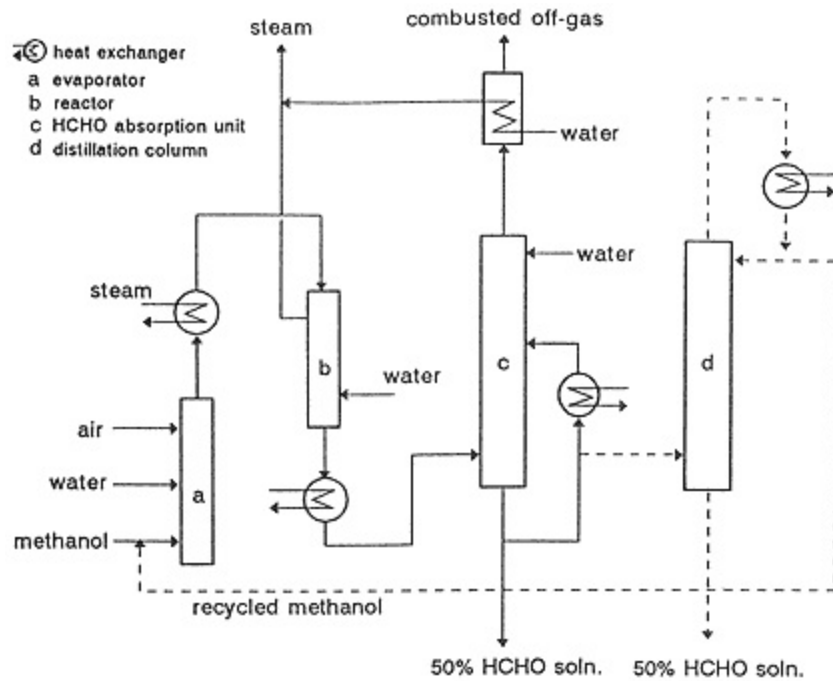


Figure 3

The methanol oxidation process. The solid lines apply to both the complete and incomplete conversion modes of operation, and the dotted lines apply only to the incomplete conversion mode of operation.

In either mode of operation, methanol, fresh air, water, and recycled off-gas are fed into an evaporator. In the incomplete conversion mode, recycled unreacted methanol is also returned to the evaporator. The evaporated mixture is further heated with steam before entering the reactor. The reaction is carried out adiabatically. The heat evolved in the exothermic oxidative reactions is used for the endothermic dehydrogenation reaction. The product from the reactor is cooled to about 150°C and sent to an absorption unit, where formaldehyde is eluted by a countercurrent flow of water.

In the complete conversion mode of operation, the absorption unit consists of multiple absorption columns with recycle of formaldehyde solution at each stage. The final product, a solution of about 5055 wt% formaldehyde, can be obtained exiting the first stage if the off-gas is recycled to reduce the use of water in the feed; otherwise, a solution containing 4044 wt% formaldehyde is obtained [18].

In the incomplete conversion mode, the mixture entering the absorption unit is a solution of about 42 wt% formaldehyde and containing methanol. The bulk of the methanol, formaldehyde, and water exits the first stage of the unit. The mixture is fed into the distillation column, from which a bottom product containing up to 55 wt% formaldehyde and less than 1 wt% methanol is obtained. The formic acid content in this bottom product is reduced by using an anion-exchange unit. The methanol in the overhead product is recycled and mixed with the fresh feed. The off-gas from the absorption unit is combusted to remove the residual methanol and other organic species. Part of it is then recycled into the reactor as inert diluent.

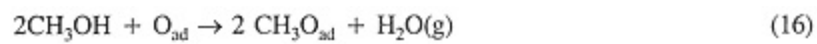
One difference between the two modes of operation is the reaction temperature. The complete conversion mode operates at a slightly higher temperature (680/720°C), whereas the incomplete conversion mode operates at 600/650°C. The lower temperature of the latter mode, coupled with the lower oxygen-methanol ratio, reduces the extent of the undesirable overoxidation reactions [Eqs. (14) and (15)]. The complete conversion mode is used in the BASF process and has an overall yield of 89.5/90.5 mol%, whereas the incomplete conversion mode is used in the ICI, Bordena, and Degussa processes and has an overall yield of 91/92 mol% [17].

A silver catalyst is used in both processes in the form of either a wire gauze or pellets. The catalyst bed is shallow, less than 50 mm thick. It has a useful life of 38 months. It is easily poisoned by traces of transition metals, including iron [19] and sulfur.

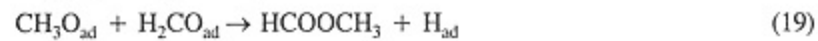
A summary of the studies of the mechanistic aspect of the catalytic reaction can be found in Reference 20. It has been confirmed that the oxidative and nonoxidative dehydrogenation reactions [Eqs. (11) and (12)] are independent processes. That is, the oxidative pathway is not simply a combination of nonoxidative dehydrogenation [Eq. (11)] followed by oxidation of hydrogen. At lower temperatures, at which the nonoxidative pathway is thermodynamically unfavorable, formaldehyde is formed only when oxygen is present on the silver catalyst [21]. Adsorbed oxygen on silver promotes the adsorption of methanol. In a low-pressure laboratory study, it was found that methanol did not adsorb on a clean silver surface but only on a silver surface containing adsorbed oxygen [22]. Oxygen adsorbs as atomic oxygen on a clean silver surface at room temperature and above, although the sticking coefficient is low (that is, a large number of collisions with the surface are needed before a molecule of oxygen adsorbs). At high pressures of oxygen, molecularly adsorbed oxygen may also be present [20].

On a silver surface with adsorbed oxygen, methanol adsorbs to form water and adsorbed methoxy [ $\text{CH}_3\text{O}_{\text{ad}}$ , Eq. (16)] [22]. The methoxy species de-

composes readily on heating to form formaldehyde and adsorbed hydrogen [Eq. (17)].



If adsorbed oxygen is depleted, the adsorbed hydrogen can react with adsorbed methoxy to produce methanol [Eq. (18)]. A small amount of by-product methylformate ( $\text{HCOOCH}_3$ ) can also be formed by the reaction of adsorbed methoxy and formaldehyde [Eq. (19)]. Adsorbed formate can be formed by reaction of adsorbed formaldehyde and adsorbed oxygen [Eq. (20)] [22,23].



The combustion product  $\text{CO}_2$  is believed to form by both direct combustion of methanol and subsequent oxidation of formaldehyde.

## 5.2.2

### Iron-molybdenum Mixed-oxidecatalyzed Process

This oxide-catalyzed process operates at a much lower temperature of 270-400°C than the silver-catalyzed process, and its feed has a lower methanol-air ratio, which is below the lower flammability limit (6.7 vol% methanol in air). The methanol concentration can be increased without danger of explosion if the oxygen concentration is reduced to below 10 mol% by diluting with recycled off-gas [24]. The amount of air used is in excess of the stoichiometric ratio. Methanol is produced by the highly exothermic oxidative dehydrogenation reaction [Eq. (11)]. The conversion of methanol is essentially complete (98-99%). The exothermicity of the reaction makes it very important to control the temperature in the reactor to avoid the development of hot spots, which enhance the undesirable side reactions of combustion of methanol and formaldehyde [Eqs. (14) and (15)].

A number of companies have developed processes using the oxide catalyst. They include Haldor-Topsøe, Perstorp/Reichhold, Lummus, Montecatini, Hiag/ Lürgi, and Nippon Kasei Chemical [17,25]. The process schematic for the oxide process is similar to that of the silver-catalyzed process operated in the complete combustion mode. Thus Figure 3 can be used to show the general features of this process. The one major difference between a silver-catalyzed and an oxide-catalyzed reaction is the reactor. In the oxide-catalyzed process, the catalyst bed is larger, about 1 m deep. The reactor is like a shell-and-tube heat exchanger



in which the heat of reaction is carried away by an oil heat-transfer medium passing outside the tubes. Because of the higher air-methanol ratio, the process equipment must be able to handle a larger throughput than the silver-catalyzed process.

The final product contains up to 55 wt% formaldehyde and 0.51.5 wt% methanol. The overall methanol conversion ranges from 95 to 99 mol%, and the yield is 8899 mol%. References 17 and 18 provide economic comparison of the oxide- and the silver-catalyzed processes.

The current commercial catalyst is a mixed oxide of iron and molybdenum, with a molybdenum-iron ratio in excess of that required for the formation of the compound  $\text{Fe}_2(\text{MoO}_4)_2$ . For example, the Harshaw catalyst is a 3:1 mixture of  $\text{MoO}_3$  and  $\text{Fe}_2(\text{MoO}_4)_2$  [26]. Commercial catalysts are often promoted with small amounts of other cations, such as vanadium, copper, chromium, and phosphorus [17]. Promotion with chromium, for example, enhances the selectivity for formaldehyde [27]. The selectivity for formaldehyde is very high, usually in excess of 90 mol%. The catalyst is more tolerant to trace contaminants than the silver catalyst. The catalyst life is typically 1218 months [28]. Excess  $\text{MoO}_3$  is necessary to maintain catalyst life because molybdenum is loss by vaporization during operation. Thus it is believed that the excess  $\text{MoO}_3$  functions as a source to replenish the Mo loss and to serve as a structural promoter to increase the surface area of  $\text{Fe}_2(\text{MoO}_4)_3$ . However, in a laboratory test it was shown that  $\text{MoO}_3$ ,  $\text{Fe}_2(\text{MoO}_4)_3$ , and  $\text{MoO}_3/\text{Fe}_2(\text{MoO}_4)_3$  were all active and selective in the methanol oxidation to formaldehyde, although  $\text{Fe}_2(\text{MoO}_4)_3$  was two to four times more active than pure  $\text{MoO}_3$  [29,30]. Thus it is possible that the excess  $\text{MoO}_3$  is also a catalytically active phase.

The detailed method of preparation of the catalyst is also important [31,32]. Among various factors, the preparation method affects the pore size, surface area, and the distribution of iron molybdate and molybdenum oxide. These factors affect the behavior of the catalyst [33].

Laboratory tests also show that the reaction of  $\text{MoO}_3$  is structure sensitive. That is, the product selectivity is a strong function of the exposed crystal plane on which the reaction proceeds [34,35]. The (010) and the (100) planes of molybdenum oxides catalyze dehydrogenation in the presence of oxygen much more selectively than other surface planes. On supported vanadium oxide catalyst of low vanadia loadings, the reaction rate is found to be a strong function of the support [36]. The rate of reaction of methanol per vanadium ions is  $10^3$  times higher on a 1 wt%  $\text{V}_2\text{O}_5/\text{ZrO}_2$  or 1 wt%  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst than 1 wt%  $\text{V}_2\text{O}_5/\text{SiO}_2$  catalyst.

It has been shown that on a Fe-Mo mixed-oxide catalyst dimethoxymethane and dimethyl ether are significant by-products at low conversions of methanol



[29]. The selectivity for formaldehyde increases with increasing conversion. The rate-limiting step of the reaction is the breaking of the C-H bond in the methyl group. This is confirmed by observing a large deuterium kinetic isotope effect when the methyl group of methanol is labeled [37].

The oxide catalyst probably undergoes reduction and oxidation cycles during the reaction. Reduction of the catalyst on exposure to methanol has been demonstrated, defect structures are formed [38,39], and the production of  $^{16}\text{O}$ -labeled water has been observed when a feed of methanol and  $^{18}\text{O}_2$  was used.

The reaction proceeds first by dissociative adsorption of methanol on the oxide to form an adsorbed methoxy and a surface hydroxy group ( $\text{OH}_{\text{ad}}$ ), similar to Equation (16). Cleavage of a C-H bond in the methyl group produces an adsorbed formaldehyde, which desorbs to yield the observed product. Further oxidation of the formaldehyde to form a surface formate similar to that in Equation (20) eventually leads to combustion.

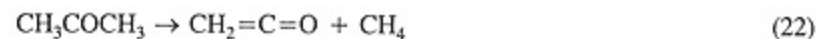
### 5.3

#### Acetic Anhydride

Acetic anhydride is the largest commercially produced carboxylic acid anhydride, with an annual U.S. production capacity of 2.6 billion lb [40]. There are three principal routes to manufacture acetic anhydride [40,41]. The older process is based on the reaction of ketene with acetic acid:

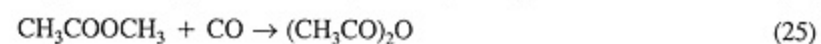


The ketene could be produced by thermal decomposition of acetone at 700–800°C or dehydration at 750°C at reduced pressure over a dehydration agent, such as triethyl phosphate:



Another process is by catalytic oxidation of acetaldehyde. Acetaldehyde is partially oxidized with air in the liquid phase to acetic acid. The acetic acid reacts with the remaining acetaldehyde to form acetaldehyde monoperoacetate, which decomposes quantitatively to acetic anhydride, acetic acid, and water.

A newer process was brought on-stream in the early 1980s by Eastman Chemical Company: catalytic carbonylation of methyl acetate produced by methanol acetylation [41,45]. The overall reaction of this process is



The reaction is catalyzed by a rhodium catalysts, with iodide and lithium salt as cocatalysts. This process currently represents about two-third of the U.S. production capacity [41].

The Eastman Chemical process for carbonylation of methyl acetate starts with the production of syngas from gasification of coal. The purified syngas is then converted to methanol over a conventional methanol synthesis plant. The conversion of methanol and acetic acid to methyl acetate [Eq. (24)] involves a novel reactor-separation column design [42]. This is necessary because methyl acetate forms an azeotrope with water and methanol. In this novel design, shown schematically in Figure 4, reaction between methanol and acetic acid occurs in the reaction section in a series of countercurrent flashing stages. Above the reaction section, water and methanol are extracted with acetic acid, and acetic acid is separated from methyl acetate. Below the reaction section, methanol is stripped from water.

In the carbonylation section, carbon monoxide, hydrogen, methyl acetate, and acetic acid solvent are fed into the liquid-phase reactor operated at over 5 MPa (50 atm) and 175°C [42]. The catalyst consists of a rhodium salt, methyl

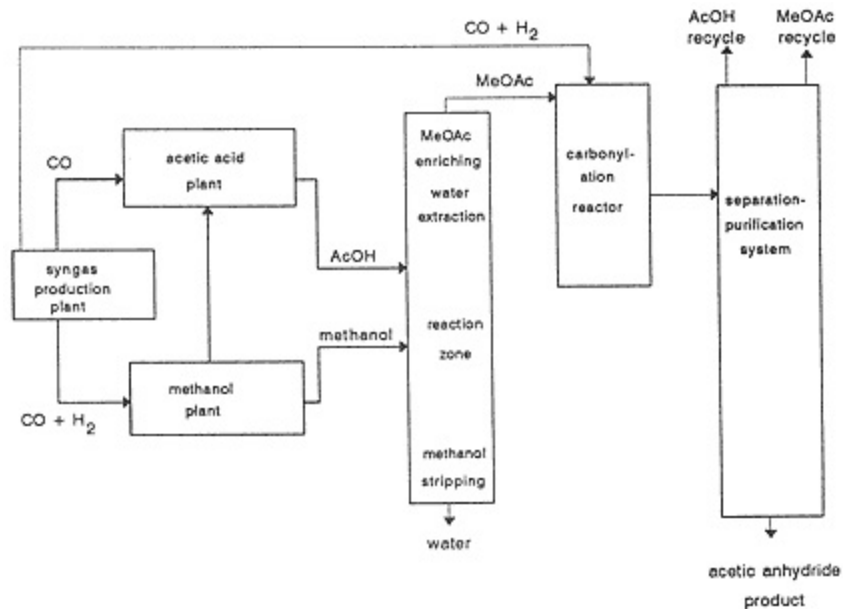


Figure 4  
The Eastman Chemical acetic anhydride production process.

iodide, and lithium iodide. Similar to the Monsanto acetic acid process, many different rhodium salts and compounds are nearly equally effective catalysts.

Although this process shows similarities to the Monsanto process for the carbonylation of methanol to produce acetic acid (Sec. 5.1.1), there are some important differences. In addition to the difference in the catalysts and the corresponding mechanistic aspect of the reactions, the methyl acetate carbonylation reaction [Eq. (25)] has a much smaller Gibbs free energy change than the methanol carbonylation reaction [Eq. (1)]. Thus, to maintain a substantial net rate of reaction, the methyl acetate carbonylation process is operated at 175–190°C up to a conversion between 50 and 70% and at over 5 MPa pressure (50 atm). Acetic anhydride is separated from the rest of the material in the effluent of the reactor by a series of distillation steps. Acetic acid is a by-product. Most of the other material in the reactor effluent is recycled back to the reactor. A small amount of tar is removed. In this process, acetic anhydride with purity up to 99.7% could be obtained. The main impurity is acetic acid.

The minor by-products of the process include ethylidene diacetate (1,1-diacetoxyethane), acetone, carbon dioxide, methane, and tar. The rhodium trapped or bound to the nonvolatile tar must be recovered for process economic reasons. The quantities of the organic products are very small. Carbon dioxide is formed by degradation of acetic anhydride.

Recovery of rhodium is an important component of the process. One example of the method to accomplish this, which was disclosed by Hembre and Cook [46], is described in Reference 44. The rhodium complex in methyl iodide is extracted into an aqueous phase using a 13% aqueous solution of hydrogen iodide. In the industrial operation, rhodium recovery of over 99.99% is achieved.

The presence of a lithium salt (LiI) as cocatalyst and hydrogen is very important for efficient production of acetic anhydride. The proposed reaction mechanism is shown in Figure 5 [42,43,47]. In this mechanism, there are two catalytic cycles for the formation of methyl acetate: a rhodium-catalyzed cycle and a lithium-catalyzed cycle. The rhodium-catalyzed cycle is similar to the Monsanto process of methanol carbonylation (Fig. 1). The participation of the second cycle was discovered when it was found that the reaction rate was much enhanced when hydrogen and a lithium salt were added [43,44]. The role of hydrogen is to reduce the catalytically inactive  $\text{Rh}(\text{CO})_2\text{I}_4$  to the active  $\text{Rh}(\text{CO})_2\text{I}_2$ . In the anhydrous medium used in the reaction, the formation of hydrogen by the reaction of carbon monoxide with water as in the water-gas shift reaction is not possible. Thus hydrogen must be added.

The dependence of the reaction rate on the concentrations of the catalysts depends on their concentrations. At high lithium concentrations, the reaction is

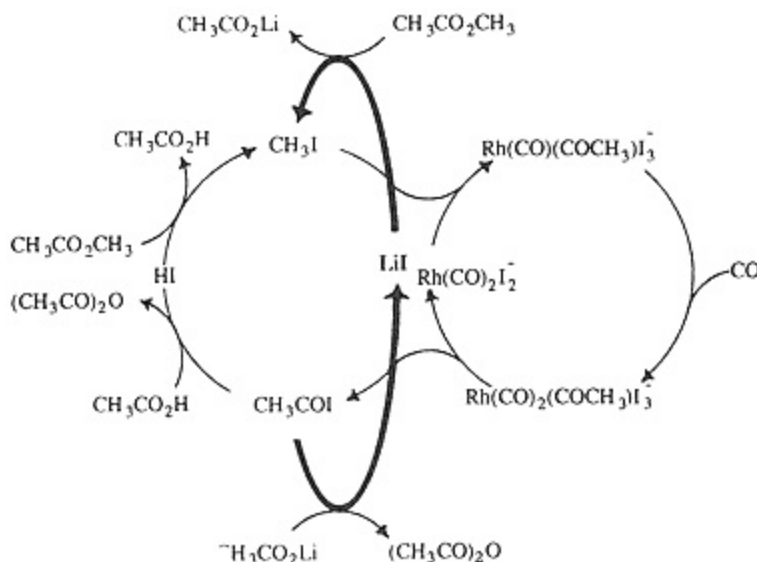


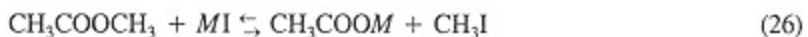
Figure 5

Mechanism of the Eastman Chemical process for the carbonylation of methyl acetate to acetic anhydride.

(Reprinted with permission from S. L. Cook, in *Acetic Acid and Its Derivative* (V. H. Agreda and J. R. Zoeller, eds.), Marcel Dekker, New York, 1993, p. 145.)

first order in rhodium and in the actual concentration of methyl iodide in the mixture. At low lithium concentrations, the rate is nearly independent of these variables. For a fixed concentration of rhodium and methyl iodide, the reaction rate increases rapidly with increasing lithium concentration until it reaches a maximum beyond which the rate is independent of lithium concentration.

Other cations also exhibit promoting effects like those of lithium, although less effective. Under one particular set of conditions, the reaction rates with promoters, relative to that without promoters, decrease as  $\text{Li}^+$ ,  $9.2 > \text{Al}^{3+}$ ,  $7.4 > \text{Na}^+$ ,  $6.3 > \text{Bu}_4\text{P}^+$ ,  $6.0 > \text{Mg}^{2+}$ ,  $5.5 > \text{Bu}_4\text{N}^+$ ,  $4.9 > \text{Zn}^{2+}$ ,  $1.4$  [44]. The enhanced rate is explained by the role of these cations in the transformation of methyl acetate to methyl iodide (M is the cation):



The forward rate of this reaction matches the observed overall rate of the carbonylation reaction.

## 5.4

### Methylated Products and Homologation to Higher Alcohols

#### 5.4.1

##### Alkylation Reactions

##### 5.4.1.1

##### Alkylation of Alkylbenzenes

The alkylation of toluene with methanol has been investigated for many years as a potential alternative route to p-xylene, ethylbenzene, and styrene. Conventional p-xylene production from petroleum reformat requires costly purification and separation from xylene isomers and other aromatics. A process that selectively produces p-xylene could have a significant commercial impact by eliminating the need for p-xylene separation. Furthermore, styrene or ethylbenzene production from methanol and toluene is desired as part of the development of processes based on C<sub>1</sub> feedstocks rather than ethylene or propylene feedstocks [48]. Para-xylene is used primarily in terephthalic acid production, a major component of polyester manufacture.

Toluene alkylation with methanol using Friedel-Crafts catalysts results in mixed products since isomerization reactions and further methylation of the desired products readily occur under these reaction conditions [49,50]. Recent work has therefore been aimed at the development of processes with high selectivity, and zeolite catalysts appear to have the most promise in this regard.

The development of ZSM-5 zeolites has had the most impact on achieving high selectivity to p-xylene from methanol and toluene. Kaeding et al. [49] showed that at 600°C and 0.1 MPa pressure, a nearly equilibrium mixture of xylenes is produced over a HZSM-5 catalyst. Under these conditions the equilibrium mixture is approximately 23% p-xylene, 51% m-xylene, and 27% o-xylene. However, if the zeolite was treated by impregnating with Mg, P, or B, the p-xylene content of the xylene product increased to >90%. Modification of the zeolite significantly decreased the activity of the catalyst, presumably a result of the B and P bonding to the framework oxygen in the zeolite. The initial toluene conversion decreased from 51% at 400°C with HZSM-5 catalyst to 40% at 600°C upon incorporation of the P. Table 2 presents a summary of some of the results reported by Kaeding et al. [49]. Operation at high toluene-methanol ratio was also necessary to limit side reactions of methanol, highly reactive on the HZSM-5 zeolites and readily converted to olefins and other hydrocarbons. Kaeding et al. [49] varied the toluene-methanol molar ratio from 1:1 to 8:1 at 600°C over the P-modified HZSM-5 catalyst and reported a decrease in the content of side products (CO, CO<sub>2</sub>, and C<sub>1</sub>C<sub>4</sub> hydrocarbons) from 5.1 wt% of the total product to 0.3 wt%. Apart from the selectivity issue, this process suffers from rapid catalyst deactivation, as shown by the data in Figure 6.

Table 2 Alkylation of Toluene with Methanol over Modified HZSM-5 Catalyst at 0.1 MPa Pressure.

Catalyst	HZSM-5	Coated HZSM-5	P-HZSM-5	B-HZSM-5
Temperature, °C	490	450	600	600
Time on-stream, h	0.5	4		56
WHSV <sup>b</sup>	20.6	15	10.3	3.8
Toluene-methanol molar feed ratio	1.5	1.4	1	2
Conversion, %				
Toluene	39	4	40	13
Methanol	+99		96	
Xylene in product, wt%	32.5	3.7	28	13.9
Xylene distribution, wt%				
Para	23	43	90	94
Meta	53	27	7	4
Ortho	24	30	3	2

a Coated HZSM-5: the zeolite was coated with Dexsil 300, a polymer with high temperature stability. P-HZSM-5: the zeolite was doped with 5 wt% P. B-HZSM-5: the zeolite was doped with B.

b Weight of toluene + methanol per hour per unit weight catalyst.

Source: Data from Kaeding et al. [49].

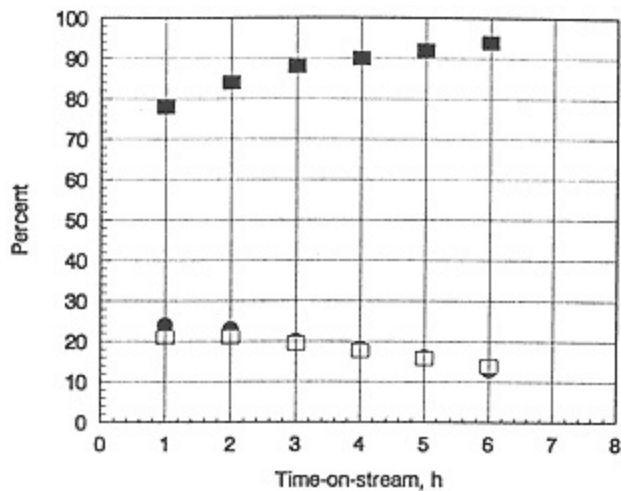


Figure 6

Catalyst deactivation during toluene alkylation with methanol over B-HZSM-5 catalyst. Temperature 600°C, WHSV = 3.8, pressure = 0.1 MPa, and toluene-methanol molar ratio = 2:1. Toluene conversion (circles); xylene wt% in organic product (open squares); and p-xylene wt% of total xylenes (filled squares).

(Data from Ref. 49.)

Kaeding et al. [49] proposed that the high p-xylene selectivity obtained with the modified zeolites was a result of steric hindrance effects within the pores of the zeolite. The first step of the reaction mechanism is thought to be methanol protonation that occurs on the Brönsted acid sites of the zeolite. This is followed by transfer of the methyl group to the aromatic ring. Alkylation at the para position is predicted to be less sterically hindered than at the meta or ortho position and is favored in the small pores of the modified zeolite. Furthermore, diffusion out of the pore by m-xylene and o-xylene would be relatively slow, resulting in isomerization of these components to p-xylene. Without modification of the zeolite, the pore dimensions are such that o-xylene and m-xylene can be produced within the pores of the zeolite [49].

Many other catalyst systems have been investigated for toluene alkylation with the aim of reducing the loss in catalyst activity that results upon modification of the HZSM-5 zeolites with Mg, B, or P. The catalysts studied are all acid and have the potential for molecular sieving to obtain high para selectivity. Examples include pillared clays [51], aluminophosphates [52], and carbon-exchanged NaY zeolites [53], as well as variously modified ZSM zeolites [54-59] and nonzeolite molecular sieves [60]. Table 3 summarizes the results of some of these studies, from which it is concluded that no significant improvement in the performance of the catalyst reported by Kaeding et al. [49] has been made to date. An additional difficulty for this potential route to p-xylene has been demonstrated by the comparative study of the performance of ZSM zeolites toward isomerization of m-xylene and toluene methylation [61]. For both reactions the activity was shown to decrease in the order ZSM-5 > ZSM-22 > ZSM-23, whereas

Table 3 Maximum Toluene Conversions and p-Xylene Selectivities  
Reported for Various Catalysts in Toluene Alkylation

Catalyst	Toluene conversion (%)	p-Xylene selectivity (%)	Reference
Na-X-zeolite	12	25	55
Mg-X-zeolite	24	40	55
ZSM-5	47	27	55
Cs-ZSM-5	15	51	55
AlPO <sub>4</sub>	13	28	52
AlPO <sub>4</sub> -Al <sub>2</sub> O <sub>3</sub>	22	24	52
Al PILCa		35	51
P-ZSM-5	40	90	49

a Al-pillared clay.



the selectivity for p-xylene followed the reverse trend. Thus the high para selectivities obtained to date correspond to catalyst activities that remain too low for commercial application of this process.

Operation with the high toluene-methanol ratios required to limit methanol side reactions means that product yield based on alkylbenzene feed is low and the reaction is limited by methanol. Attempts to overcome this limitation have been made by use of composite methanol synthesis-HZSM-5 catalysts, and this approach has been demonstrated for p-xylene alkylation to yield 1,2,4-trimethylbenzene. Yashima et al. [62] claimed that the efficiency of methanol usage as an alkylating agent is greater when the methanol is produced in situ on the Zn/Cr oxide catalyst than when the methanol is cofed with the p-xylene.

Various studies have reported the use of zeolite catalysts for the alkylation of alkylbenzenes other than toluene. Studies include the conversion of ethylbenzene and methanol to yield p-ethyltoluene, which after dehydrogenation yields p-methylstyrene. The latter compound can be polymerized to yield a polystyrene analog [63]. HZSM-5 zeolites prepared with Na, K, and Rb ions were examined by Kolboe et al. [63] who reported selectivities of 1050% for ethylbenzene alkylation with methanol. High para selectivity was observed, particularly for the Rb-containing zeolite that has a low Al content. In addition, the alkylation of phenol with methanol is a commercially viable process for the production of cresols and xlenols. The reaction occurs in the liquid phase at about 300°C and 5 MPa pressure. The catalyst is aluminum oxide, but recent work on HY and ZSM-5 zeolites has been reported that increases selectivity to p-cresol as a result of shape selectivity effects [64].

Although the para selectivity of these alkylation reactions is a result of zeolite shape selectivity effects, the acidity of the catalyst also plays an important role. According to the mechanism for toluene alkylation, for example, the methanol is protonated on Brønsted acid sites [49]. Furthermore, high catalyst acidity can increase the dehydration of methanol to water and dimethyl ether [65]. During toluene alkylation with methanol, side-chain methylation to styrene and ethylbenzene can also occur. Side-chain alkylation occurs when both acid and basic sites are available, such as with alkali-exchanged X and Y zeolites [55]. Monsanto has obtained patents describing X zeolites containing Cs and B that yielded ethylbenzene and styrene with 50% selectivity at 60% conversion of methanol [66]. A significant portion of the methanol is dehydrogenated. More recently, Zheng et al. [55] reported > 90% selectivity to ethylbenzene and styrene with a K-exchanged X zeolite at a 10% toluene conversion.

#### 5.4.1.2

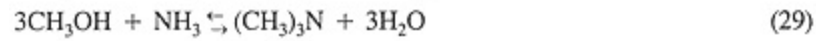
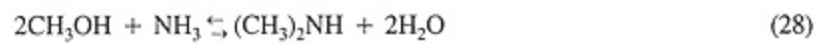
##### Alkylation of Amines and Ammonia

The production of methylamines from anhydrous ammonia and methanol is an established industrial process that consumes about 4% of the total U.S. metha-





nol production [67]. Dimethylamine (DMA) is the more desired product since about 60% of methylamine demand is for DMA [67]. However, monomethylamine and trimethylamine (TMA) are also produced at typical synthesis conditions since the reactions



approach equilibrium in the industrial process.

The conversion of methanol and ammonia to methylamines is achieved over dehydration catalysts operated in the temperature range 300–450°C and 0.12 MPa pressure. The reactions are exothermic, and excess ammonia is used to control the product distribution. The dehydration catalysts are generally promoted Si-Al composites. The promoters include molybdenum sulfide and silver phosphate [68]. In the commercial Leonard process, a gas-phase downflow catalytic reactor operating at about 350°C and 0.62 MPa is used [69]. Recovery of the desired product is achieved through a series of four distillation and extractive distillation columns. Unwanted product is recycled, suppressing further formation of the undesired component in the reactor. A very small amount of methanol is lost to CO and H<sub>2</sub>, and yields from the commercial process based on methanol and ammonia are >97% [70].

In recent years research on the development of highly selective catalysts has been reported (see Table 4). In this approach, zeolite catalysts that selective-

Table 4 Catalyst Performance Data for Methylamine Synthesis

Catalyst	Methanol/ NH <sub>3</sub> ratio <sup>a</sup>	Temperature (°C)	Methanol conversion (%)	MMA <sup>b</sup> (%)	Selectivity			Reference
					DMA (%)	TMA (%)	DME (%)	
SAPO-34	1:1	325		63	32	5		122
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	1:1	300/400	>90	18	11	45	27	72
Si-H- mordenite	1:1	300/400	>90	33	65	1	<1	72
γ-Al <sub>2</sub> O <sub>3</sub>	1:1	400	79	4	4	0	92	71
SiO <sub>2</sub> -MgO	1:1	400	66		12	82	2	71
La- Mordenite	1:1	400	95	20	59	20	1	71

<sup>a</sup> Molar feed ratio of CH<sub>3</sub>OH:NH<sub>3</sub>.

<sup>b</sup> Monomethylamine.

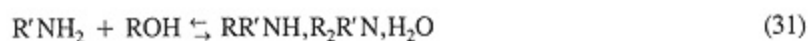
ly produce DMA or monomethylamine, partly because of the shape selectivity properties of the zeolites, are being studied. Mochida et al. [71] reported the suppression of TMA selectivity to less than 10% of the total methylamine product using alkali-earth ion-exchanged zeolites. For example, a La-exchanged synthetic mordenite zeolite (Norton zeolon with 50% H<sup>+</sup> exchanged with La<sup>3+</sup>) operated at 300°C and 0.1 MPa pressure with 7% methanol and 7% ammonia in He, resulted in 85% selectivity to DMA and monomethylamine at 36% methanol conversion. The low TMA selectivity was ascribed to the 0.39 nm free diameter of the zeolite compared with the estimated minimum molecular sizes of 0.39, 0.30, and 0.22 nm for TMA, DMA, and monomethylamine, respectively [71].

A similar shape selectivity was reported in the more recent study of modified mordenite, faujasite, and ZSM-5 zeolites by Segawa and Tachibana [72]. The mordenite zeolites, treated with SiCl<sub>4</sub> at 973 K in Na form and then exchanged to protonic form, gave 98% selectivity to monomethylamine and DMA, with <1% diethyl ether (DME) as a side product, at a methanol conversion > 90%. The reaction was performed with a feed of composition NH<sub>3</sub>/CH<sub>3</sub>OH/ N<sub>2</sub> = 1:1:31 mol% at atmospheric pressure and in the temperature range 300-400°C. The formation of TMA is limited by the catalyst pore openings, which were smaller than the TMA molecule. Under the conditions of the laboratory experiments, no catalyst deactivation was observed [72].

In addition to the production of methylamines, the formation of alkylamines from ammonia and alcohols is well known. Substituted amines can also be generated according to the reactions:



and



where R and R' are alkyl groups. The synthesis is carried out at elevated pressures (0.12 MPa) on dehydration oxide catalysts, supported group VIII metal catalysts, and Cu-based catalysts. Reaction temperatures are typically 350-450°C for the oxide catalysts and 170-220°C for the supported metal catalysts. A variety of different catalysts and feedstocks have been investigated and are summarized by Herman [73]. Selectivity control is also an important issue in this process. Ford and Johnson [74] showed that strontium hydrogen phosphate catalyst is selective in converting methanol and ethylamine to methyl- and dimethylethylamine (>90%), which is far removed from the equilibrium product mixture.

## 5.4.2

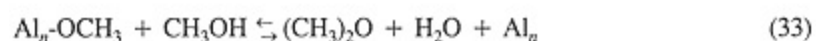
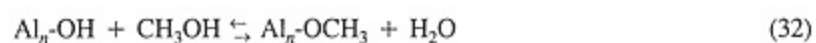
### Dehydration:

#### Synthesis of Dimethyl Ether

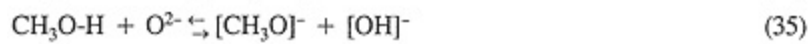
Dimethyl ether is an important intermediate in several processes converting C<sub>1</sub> feedstocks to liquid fuels or chemicals. DME may also be used as an alternative propellant for aerosols [67]. It is well known that DME can be produced from methanol over acid dehydration catalysts under relatively mild conditions. Most of the investigations reporting DME formation are related to olefin and gasoline production via the Mobile methanol-to-olefins and methanol-to-gasoline processes, discussed in Chapter 4. In both cases, elevated pressures (13 MPa) and temperatures above 300°C are used to maximize olefin and aromatic yield. In this section DME production from methanol is considered in the context of producing DME as a useful chemical rather than as an intermediate in a Mobil process.

Methanol dehydration to DME as described in patent literature occurs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with phosphates or titanates [75]. Temperatures in the range 250–400°C and pressures up to 1.04 MPa have been claimed. Many other catalysts have been reported for alcohol dehydration, including zeolites, silica aluminas, mixed metal oxides, and ion-exchange resins, and these catalysts were reviewed recently [65,76]. DME formation has also been reported over a 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst with a 90% selectivity at 71% methanol conversion [77]. The reaction was performed at 200°C and 0.1 MPa. When the Pd was supported on ZnO, the product was primarily methyl formate, whereas on various other supports, including SiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and MgO, only CO was produced.

Both Lewis and Brønsted acidity are involved in the dehydration reactions over acid catalysts, and selectivity control to limit the dehydration of DME to olefins and aromatics requires that the surface acidity not be too high and the reaction temperature be below 300°C [65]. The olefins are generally thought to be produced by a consecutive reaction in which methanol is first converted to DME, which in turn is converted to olefins and aromatics. Reaction mechanisms for DME formation have been proposed by various investigators. According to Kubelkova et al. [78], the mechanism over Si-Al zeolites involves protonation of the hydroxyl group of methanol on a Brønsted acid site to form a skeletal methoxyl. This methoxyl group reacts with a gas-phase methanol molecule to form DME at 180–300°C and C<sub>2</sub>–C<sub>5</sub> aliphatics and aromatics above 300°C. According to these authors, Lewis acid sites (Al<sub>n</sub>-OH), associated with nonskeletal alumina, can also form methoxyls according to the reaction



Bandeira and Naccache [79] proposed a dual acid-base mechanism in which CH<sub>3</sub>OH reacts on a Brönsted acid site and another methanol molecule reacts at an adjacent O<sub>2</sub>-site. Thus a bimolecular Langmuir-Hinshelwood reaction mechanism is proposed according to the following reaction steps:



and reaction (37) is the rate limiting step.

Most recently, methanol dehydration kinetics were examined over a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 0.15 MPa in the temperature range 290–360°C. A kinetic equation assuming surface reaction control with dissociative adsorption of methanol gave the best fit to the experimental results [80]. The dissociative adsorption is consistent with many previous kinetic models in which the rate of DME formation is found to be proportional to the square root of the methanol concentration [80].

A high selectivity to DME can be obtained by suitable choice of the catalyst and the reaction conditions. It has been shown that weak acid sites favor methanol dehydration [81] and that strong acid sites, although having high turnover frequency, are less selective than weak acid sites [65]. Controlled dealumination of the zeolite is therefore one way of achieving high DME selectivity. DME selectivity and yield have also been shown to increase with time on-stream, presumably because of coking of the strong acid sites, as shown by the data in Table 5 for a SAPO-11 catalyst [82]. Acidity control is most effective with zeolite catalysts, and these appear to be the most promising catalysts for this synthesis.

Table 5 Effect of Coking on Dimethylether Yield over SAPO-11 Catalysts

	Methanol feed rate (g methanol/g/h)			
	0.050	0.050	0.031	0.031
Time on-stream, h	0.12	1.1	0.17	1.5
Methanol conversion, %	43.4	35.3	68.0	38.9
DME selectivity, %	41.2	67.1	5.1	86.6
DME yield, %	17.9	23.7	3.5	33.7

Source: Adapted from Reference 82.

A single-step process for DME production from synthesis gas in which methanol is a co-product was also investigated recently [8385]. The methanol synthesis, methanol dehydration, and water-gas shift reactions occur simultaneously in the reactor over mixed methanol and alcohol dehydration catalysts. The Air Products slurry-phase process has been tested over a wide range of operating conditions and offers the potential for both lower capital and operating costs compared with a multistep process in which methanol synthesis from synthesis gas is the first step of the process [83,85]. Most recently, a DME to methanol selectivity of 76:24 mol% was claimed for a mixed-catalyst system operated at 250°C and 65 mol% CO conversion [84]. The productivity at these conditions was 4.7 gmol/kg/h of DME and 1.5 gmol/kg/h of methanol. These values compare with 95% DME selectivity and 51% methanol conversion over a SAPO-16 catalyst at 425°C for the synthesis of DME from methanol [86].

### 5.4.3

Dehydrogenation:

Synthesis of Methyl Formate

There has been significant interest in studying the dehydrogenation of methanol to methyl formate (MF) as a potential industrial process [87]. The overall stoichiometry for this reaction may be written as



However, the reaction is thought to occur in two steps via formaldehyde that subsequently converts to methyl formate by the Tischenko mechanism [88]. The reaction occurs on various copper-containing catalysts [8792] and was recently shown to occur over Pd catalysts [77]. With Pd, however, the selectivity to methyl formate is very dependent on the support, as shown by the comparative data in Table 6. Selectivity is >90% to CO over most of the Pd catalysts; however, with a 1 wt% Pd/ZnO catalyst, the selectivity is 80% to methyl formate at a methanol conversion of 21% [77]. On copper catalysts, 93% selectivity to MF has been claimed at 50% methanol conversion and reaction temperatures 285330°C [87].

The catalyst support has also been shown to play an important role in methanol dehydration to MF [93], particularly over the copper catalysts. Tonner et al. [88] investigated the copper supported on chromia, magnesia, and silica for methanol dehydrogenation and obtained a range of conversions (431%) and MF selectivities (6295%), depending on the support. The support effect was thought to be related to reduced copper activity as a result of a copper-support interaction. Alternatively, a local excess of hydrogen adsorbed on the support could reduce the yield of MF by favoring the reverse of reaction (38). Tonner et al. [88] have shown that the catalysts with high Cu dispersion and bulk density gave the maximum activity per unit volume of catalyst. An 86% selectivity to MF



Table 6 Comparative Performance of Catalysts for Methanol Dehydration and Dehydrogenation

Catalyst	Conversion (%)	Selectivity <sup>a</sup> (%)		
		CO	MF	DME
Pd/ZnO	21	20	80	0
Pd/SiO <sub>2</sub>	2	100	0	0
Pd/Al <sub>2</sub> O <sub>3</sub>	71	10	0	90
Pd/MgO	11	100	0	0
Cu/SiO <sub>2</sub>	18	6	94	0

<sup>a</sup> MF = HCOOCH<sub>3</sub>; DME = (CH<sub>3</sub>)<sub>2</sub>O.

Source: Adapted from Reference 77.

and a 2% methanol conversion were reported at 270°C and 0.1 MPa. Significant catalyst deactivation was reported for an unsupported Raney Cu catalyst, apparently because of polymerization of the formaldehyde intermediate [88].

Methyl formate can also be produced by carbonylation of methanol according to the reaction



This reaction occurs at high pressure (810 MPa) in the presence of a catalyst, such as sodium methoxide, at low temperature (80°C) [87]. The effects of various alkali metal alkoxides has been investigated, and the activity of the catalyst has been shown to increase with increasing ionization potential of the metal [94]. From kinetic studies it has also been shown that both CO<sub>2</sub> and H<sub>2</sub>O react with the catalyst, resulting in a reduced reaction rate. The effect of CO<sub>2</sub> is twice as severe as that of water [95].

The proposed commercial unit for this process operates with about 2 wt% catalyst in a "loop reactor," designed to have efficient heat transfer and gas-liquid dispersion [93]. The CO and methanol conversions are 95 and 30%, respectively, with MF production of approximately 800 g/h/L [87]. The process has been proven on the pilot scale [93].

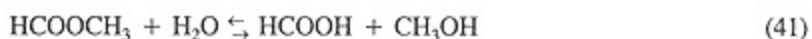
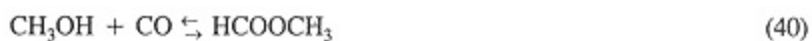
The methanol dehydrogenation route to MF has not been commercialized, and the lifetime of the acid catalysts has not been reported. However, the process is attractive since it operates at low pressure compared with the carbonylation route. Technical development of the carbonylation route is far more advanced than that of the dehydrogenation route, in part because of the interest in meth-



anol carbonylation to methyl formate with subsequent hydrogenolysis as an alternative low-temperature methanol synthesis route [96,97].

Production of methyl formate from methanol also leads to the potential production of formic acid from methanol [87]. Formic acid is produced commercially as a side product of the liquid-phase oxidation of n-butane to acetic acid. It has been suggested, however, that new formic acid capacity will best be obtained by hydrolysis of methyl formate because of raw material costs [87]. The methyl formate could be produced by either the carbonylation or dehydration of methanol according to the technologies discussed previously.

The Scientific Design/Bethlehem Steel process for formic acid production is based on the methanol carbonylation route to methyl formate [87,98,99]. The methyl formate is subsequently hydrolyzed and the products separated to yield pure formic acid and methanol. The methanol is recycled to the carbonylation reactor, and overall methanol usage is about 2 kg per 100 kg product [99]. The reaction of methyl formate and water to form formic acid is an equilibrium reaction performed at 0.3 MPa and 80°C, with a residence time of about 1h [87]. The overall process stoichiometry yields formic acid from CO and H<sub>2</sub>O according to the reactions



#### 5.4.4

##### Methanol Homologation

Methanol homologation to higher alcohols, in which the carbon being added to the alcohols comes from methanol, has been claimed in a noncatalytic reaction with metal acetylides [100]. For example, the reaction of methanol and CeC<sub>2</sub> at 400°C and 0.1 MPa yielded alcohols up to pentanols, with a maximum selectivity for 2-methyl-1-propanol of 77%. The product distribution included a mixture of alcohols, CO, H<sub>2</sub>, and CH<sub>4</sub>.

Depending on the contact time in the laboratory-scale test reactor, ethanol selectivities ranged from 1.3% (C atom) to 12.5% and 2-methyl-1-propanol selectivities ranged from 58 to 86%. Methanol conversion was <2%. Using <sup>13</sup>C-labeled methanol, Fox et al. [101] showed that methanol rather than the metal acetylide was the source of carbon in the higher alcohols. A formaldehyde condensation reaction mechanism has been invoked to explain the <sup>13</sup>C distribution in the product.

Accordingly, methanol reacts with the metal acetylide to form metal methoxide and acetylene. The methoxide decomposes to formaldehyde, which undergoes a condensation reaction to yield acetaldehyde. Hydrogenation of the acetaldehyde yields ethanol. Similar aldol condensation reactions occur among the aldehydes with carbon number ≥ 1 to yield higher alcohols.

Methanol homologation to produce higher alcohols has also been invoked in the synthesis of higher alcohols from CO/CO<sub>2</sub>/H<sub>2</sub> over alkali-promoted Cu/ZnO and Zn/Cr catalysts [102,104]. In both cases the reaction is carried out at high pressure (>7.5 MPa) and high temperatures (250–325°C for the Cu/ZnO catalyst and 300–400°C for the Zn/Cr catalyst). The product obtained from this synthesis is a complex mixture of alcohols, aldehydes, esters, and hydrocarbons, the relative amounts of each being very dependent on the catalyst and the operating conditions [102,104]. The product alcohols are primarily 2-methyl branched and linear alcohols. Various investigators have shown that addition of alkali metal salts, such as K<sub>2</sub>CO<sub>3</sub> and CsOH, increases the selectivity to the higher alcohols, as does operation with low ratio synthesis gas (H<sub>2</sub>/CO < 1) [102,106]. This technology offers a route to an oxygenate mix suitable for blending with gasolines, and commercial processes have been proposed [107,108].

Based on mechanistic and kinetic studies of the higher alcohol synthesis from synthesis gas, it has been shown that the ethanol in the mixed-oxygenate product is produced from intermediates derived from methanol, not CO [103,109]. Kinetic models of the synthesis have been developed that are able to explain the observed product distribution [110,111]. These models are based on a detailed understanding of the reaction mechanism in which two types of reactions dominate: aldol condensation, which yields primarily 2-methyl branched alcohols, and C<sub>1</sub> coupling reactions, which yield linear alcohols [106,111]. Estimates of the parameters of the kinetic models that quantitatively describe the oxygenate product distributions suggest that the rate of ethanol formation is about an order of magnitude lower than the rate of production of branched alcohols [111,112]. On the Cs/Cu/Zn catalysts, this results in a minimum in yield of ethanol compared with the yields of methanol, 1-propanol, and 2-methyl-1 propanol. Although methanol conversion to ethanol has been confirmed as part of the higher alcohol synthesis from synthesis gas, this synthesis does not offer a plausible route for the conversion of methanol to ethanol. Under the reaction conditions methanol rapidly decomposes, even at a pressure of 0.1 MPa [113], to yield an equilibrium mix of methanol, CO, and H<sub>2</sub>. Furthermore, as shown by the data in Table 7, the yield of ethanol remains low even with methanol in the feed.

Higher alcohol formation from synthesis gas is also known to occur over MoS<sub>2</sub>-based catalysts. The alcohol product distribution is quite different from the modified methanol synthesis catalysts and consists primarily of linear alcohols [114]. In particular, the product distribution with Cs/Co/MoS<sub>2</sub> catalysts has a maximum in the yield of ethanol [115]. A modification of this synthesis in which higher alcohols formed from methanol and synthesis gas has been claimed by Quaderer et al. [116]. As K<sub>2</sub>CO<sub>3</sub>-promoted CoS/MoS<sub>2</sub> catalyst, operated at

Table 7 Higher Alcohol Yields over K/Cu/Zn Oxide Catalyst with Methanol in the Feed<sup>a</sup>

Space velocity, h <sup>-1</sup>	2300	2800
Methanol in feed, %	0	8.6
Yields, g/kg/h		
Methanol	118	
Ethanol	8	16
1-Propanol	5	10
1-Butanol	2	1
2-Methyl-1-propanol	4	4

<sup>a</sup> Temperature 285°C, pressure 10.4 MPa, feed H<sub>2</sub>/CO = 0.9.

Source: Adapted from Reference 112.

290°C and 13.7 MPa, yielded a product with significant ethanol content, as shown by the data in Table 8. This process is similar to the higher alcohol synthesis over promoted Cu/Zn and Zn/Cr catalysts; however, the rate of ethanol formation is significantly greater with the MoS<sub>2</sub>-based catalysts than with the modified methanol synthesis catalysts.

Methanol can also be converted to ethanol by homologation with H<sub>2</sub> and CO in the presence of cobalt-carbonyl complexes. As pointed out by Wender, however, the reaction  $\text{CH}_3\text{OH} + \text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}$  is reductive carbonylation of methanol rather than homologation [117]. The reductive carbonylation of methanol to ethanol has been known for many years, and various reviews of the process and catalysts have been published [117-119].

Reductive carbonylation of methanol based on homogeneous cobalt catalysts can yield a complex mixture of higher alcohols, aldehydes, esters, acids, and

Table 8 Higher Alcohol Synthesis from Methanol and Synthesis Gas over K/CoS/MoS<sub>2</sub> Catalysts<sup>a</sup>

Component	Yield (g/h)
Methanol	2.73
Ethanol	5.36
Propanols	1.51
Butanols	0.38

<sup>a</sup> Temperature 290°C, pressure 13.8 MPa, gas hourly space velocity

2000 h<sup>-1</sup>; feed H<sub>2</sub>/CO = 1.05.

Source: Adapted from Reference 116.

ethers. Typically, 50-90% of the product is ethanol plus acetaldehyde with cobalt catalysts. Such promoters as iodine increase selectivity toward ethanol, whereas group V metals promote acetaldehyde formation [117]. Figure 7 presents an example of the product distribution obtained with varying amounts of iodine promoter. Hydrogenation cocatalysts also increase the yield of ethanol, ruthenium being the best. Despite these improvements, selectivity to ethanol is usually below 75% at the optimum temperature of about 200°C and high operating pressures of 27 MPa. At the present state of technical development, the process remains uneconomical, partly because of the low catalyst selectivities and activities.

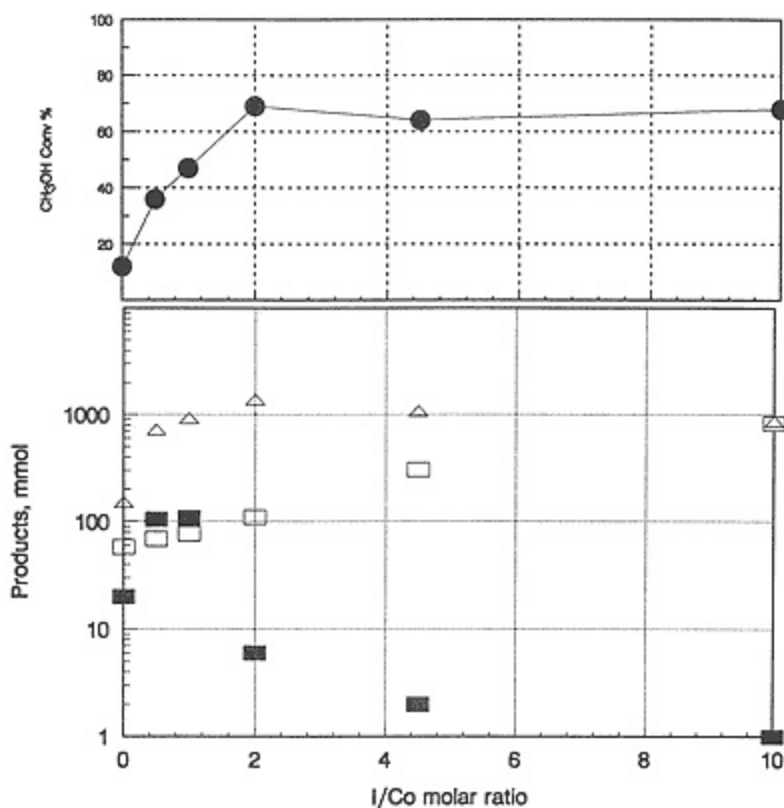


Figure 7

Effect of I/Co ratio on methanol homologation over cobalt carbonyl catalyst. Pressure = 27.3 MPa, temperature = 200°C, and H<sub>2</sub>/CO = 1. Ethanol (filled squares), dimethyl ether (open squares), and others, including CH<sub>4</sub> (triangles). (Data from Ref. 118.)

## 5.4.5 Miscellaneous Reactions

### 5.4.5.1 Methyl Methacrylate and Dimethyl Terephthalate Synthesis

Methanol is utilized in the production of methyl methacrylate (MMA), a monomer used in the manufacture of glasslike plastics [120]. The most important technology for MMA manufacture is the acetone cyanohydrin process, a mature technology in which acetone and hydrogen cyanide are the primary reactants. The acetone cyanohydrin produced from these two reactants is reacted with sulfuric acid to produce a methacrylamide sulfate. MMA is produced by reacting methanol with this sulfate. Although this technology is well established, it suffers from a negative environmental impact associated with HCN transportation and the disposal of sulfuric acid and ammonia. More recent process developments for MMA manufacture attempt to address this issue. In the alternative isobutylene technology practiced in Japan, methanol is used for the esterification of methacrylic acid to methyl methacrylate. The methacrylic acid is produced from isobutylene in a series of high-temperature catalytic oxidation reactions [120].

Terephthalic acid (TA) is a starting material for the manufacture of polyesters, used particularly in fiber manufacture. TA can be produced commercially by hydrolysis of dimethyl terephthalate, the latter compound produced by oxidation of p-xylene. Oxidation of p-xylene is achieved in the presence of Co/Mn salt catalysts that yield p-toluic acid. The oxidation is performed at 140–170°C and 0.4–0.8 MPa pressure. Esterification of the toluic acid with methanol at 250–280°C and 22.5 MPa yields TA. Alternatively, the oxidation is performed in the presence of a bromine promoter that results in the oxidation of both methyl groups to yield TA [121].

## 5.5 Synthesis of Ethers

Interest in the synthesis of ethers, particularly methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME), has increased in recent years as a result of the need for oxygenates in reformulated gasolines. The 1990 amendment to the U.S. Clean Air Act mandates that new gasoline formulations have a minimum oxygen content of 2 wt% in areas that do not comply with U.S. Environmental Protection Agency attainment standards for ozone or CO. Ethers, particularly MTBE, reduce CO emissions during cold weather [123,124], and they are at present the oxygenate of choice to meet the oxygenate requirement of reformulated gasolines [124]. Ethers are preferred over other oxygenates, such as alcohols, because of their favorable vaporization properties and low sensitivity

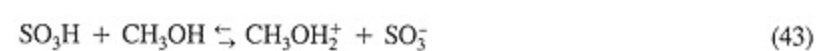
to water [124]. However, recent health concerns related to the use of MTBE have been raised that could impact on its future use [123].

Although MTBE is generated as a by-product of propylene oxide production [125], direct synthesis by acid-catalyzed addition of methanol to isobutylene is necessary to meet the rapid increase in worldwide MTBE demand. Worldwide capacity of MTBE is expected to double by 1995 from the 1992 level of 377,000 bbl/day [125,126], and much of this increased capacity is expected to come from new plants and MTBE expansions [126].

Commercial MTBE (and TAME) synthesis occurs at about 1.5 MPa and 100°C in the liquid phase over an acid resin catalyst that is based on the sulfonic acid group -SO<sub>3</sub>H. The synthesis reaction is slightly exothermic and limited by equilibrium under the conditions of the commercial operation:



The reaction mechanism and kinetics of the MTBE synthesis from methanol and isobutylene have been studied over the commercial Amberlyst 15 cation-exchange resin catalyst. An activation energy of 71.2 kJ/mol was reported by Ancillotti et al. [127] for the forward reaction, whereas Gicquel and Torck [128] reported a value of 82.0 kJ/mol. For the reverse reaction an activation energy of 122.6 kJ/mol has been reported [128]. The kinetics of the reaction are very dependent on the olefin and alcohol concentration. Ancillotti et al. [129] showed that the initial rate of synthesis is zero order in methanol at methanol-isobutylene ratios > 1. Most commercial processes operate at close to the stoichiometric ratio, and the rate is first order in isobutylene under these conditions. Ancillotti et al. [129] suggested that the effect of alcohol-olefin ratio can be explained in terms of the equilibrium reaction



The kinetics are consistent with an ionic mechanism wherein the rate-determining step is the protonation of the olefin by the solvated proton. At lower alcohol-olefin ratios (<1), the order of reaction is negative in the alcohol, reaction (43) is shifted to the left, and the olefin is protonated directly by the sulfonic acid group of the resin. A Langmuir-Hinshelwood model of the kinetics was also described by Gicquel and Torck [128] for relatively high methanol concentrations.

Commercial MTBE (and TAME) processes are very similar and based on the acid-catalyzed addition of methanol to isobutylene. The reactor effluent is fractionated in various stages to recover MTBE, methanol for recycle, and unreacted C<sub>4</sub> hydrocarbons present in the feed. The three different designs of the commercial processes reflect different approaches to control the heat gen-

erated by the reaction [130,132], since the resin catalysts are very temperature sensitive and must be operated below about 90°C. The fixed-bed reactor with recycle was the first process commercialized [130]. In this process methanol and isobutylene are premixed and heated before being fed to a fixed-bed reactor. The reaction exotherm heats the reacting fluid, and the effluent from the reactor is split into two streams. Part of the effluent is recycled back to the first reactor, and part undergoes further conversion in a second reactor. In this way the reactor temperature is controlled. The fractionation of the product from the second reactor occurs in a single column to recover the MTBE. The overhead from this column is further treated in a methanol wash column and a methanol fractionation column to recover C<sub>4</sub> raffinate (unreacted hydrocarbons in the isobutylene feed) and methanol for recycle [130].

For the fixed-bed tubular reactor, the reaction exotherm is controlled by placing the catalyst in a series of tubes. The heat generated by reaction in the tubes is removed by circulating cooling water on the shell side of the reactor. The effluent from this reactor passes to a second packed-bed reactor for further conversion. Product recovery follows the same flow scheme as for the packed-bed reactor with recycle [130].

A more recent innovation in MTBE synthesis is the use of catalytic distillation in which the reactor and MTBE fractionator are combined in one vessel [130,131]. The reactive distillation unit is basically a tray distillation column with catalyst held in a proprietary packing placed on the trays. In this way the heat of reaction is recovered and used for the distillation and recovery of the MTBE. Among the major benefits of this design are efficient conversion of the isobutylene [130] and lower operating and capital costs [131]. Many processes based on this technology have been established recently [126,132].

Efficient utilization of the olefin feedstock is critical in ether production because of the limited supply and cost of the olefin feedstock [133]. The estimated order of magnitude cost of a 12,500 bpsd MTBE complex is about \$200 million (1992 dollars), of which 3550% of the cost is associated with dehydrogenation costs for isobutylene synthesis from isobutane [130]. The source of olefins is a major issue in ether production [134,136], and the interest in TAME and other ethers for fuel oxygenates stems from the fact that they can be produced from methanol and olefins other than isobutylene [134].

The synthesis of ethers at high temperature using zeolites was also investigated recently [137,139]. Use of shape-selective ZSM-5 and ZSM-11 zeolites almost eliminates the unwanted side product diisobutene [137]. The reaction temperature is above 100°C with zeolites, and the synthesis reaction occurs in the gas phase. Table 9 compares MTBE synthesis over a zeolite catalyst with that over the Amberlyst 15 resin catalyst. Advantages of zeolites compared with



Table 9 Comparison of MTBE Synthesis over Zeolite and Amberlyst 15 Catalysts

	Amberlyst 15	H-ZSM-5	
Temperature, °C	75	75	115
W/F, g-h/mola	20	16.1	18.9
Isobutylene conversion, %	94.9	35.2	84.2
Selectivity to MTBE, %	98.1	100	100

a Catalyst weight to feed flow rate.

Source: Adapted from Reference 138.

the commercial process using acid resin catalysts include the high thermal stability of the zeolites, no acid effluent, high MTBE selectivity, and less sensitivity to the alcohol-olefin ratio in the reactor [137]. However, the zeolites are less acid than the Amberlyst 15 commercial catalysts and have a lower acid site density. Comparing the performance of the catalysts at low temperature, at which the resin catalyst is stable, shows the zeolite to be about 10 times less active than the resin catalysts [138]. Attempts to increase the zeolite acidity with triflic acid have not been successful, since the active sites are blocked by the acid added to the zeolite [140].

Although MTBE synthesis from methanol and isobutylene is a well-established commercial process, shortfalls in olefin feedstock have led to studies aimed at alternative routes to MTBE. The direct coupling of methanol and 2-methyl-1-propanol to yield methyl isobutyl ether (MIBE) has been demonstrated over resin catalysts [141,142]. Over a Nafion H resin at 157°C, Nunan et al. [141] reported high selectivity for MIBE from methanol and 2-methyl-1-propanol (42 mol% of product mix). Air Products and Chemicals have also reported the synthesis of ethers from methanol-isobutanol, the latter produced from synthesis gas (CO/ CO<sub>2</sub>/H<sub>2</sub>) over Cs/Cu/ZnO catalysts [143]. In this case, the reaction occurs in a slurry reactor and the feedstock is synthesis gas. Laboratory studies of MTBE synthesis via the oxidative coupling of methane have also been reported [144]. However, yields of these process are very low and require more development before they can be considered alternatives to current commercial technology.

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## 6

## Fuel Methanol

Glyn D. Short

ICI Americas, Wilmington, Delaware

## 6.1

## Foreword

Between 1990 and 1992, the U.S. Congress passed two landmark bills, the Clean Air Act Amendments (CAAA) of 1990 and the Energy Policy and Conservation Act (EPACT) of 1992. These two bills will slowly change the nature of transportation fuels and the engines they power, not only in the United States, but eventually throughout the world. The CAAA, with its emphasis on achieving even stricter emissions limits for all classes of road vehicles, will engender redesign and optimization of cost-effective emissions control systems for both gasoline and diesel. The EPACT specifically excludes gasoline and diesel from consideration as alternative fuels, which are mandated for use in an increasingly large fraction of the federal fleet to promote energy security (Table 1). In addition, the President of the United States, in 1993, formed a Task Force for Alternative Fuels with the assigned role of expediting the conversion of the federal fleet as well as facilitating the proliferation of alternative fuels into the private sector.

The views expressed in this chapter are those of the author, not ICI.

Table 1 EPACT-Mandated Public Sector Alternative Fuel Fleet Vehicle Purchases

Year	Federal (%) <sup>a</sup>	State (%)	Fuel providers (%)
1993	5,000		
1994	7,000		
1995	10,000		
1996	25	10	30
1997	33	15	50
1998	50	25	70
1999	75	50	90
2000	75	75	90
2001	75	75	90
2002	75	75	90
2003	75	75	90
2004	75	75	90
2005	75	75	90
2006 on	75	75	90

<sup>a</sup> Values for 1993-1995 are not percentages.

Of singular importance to the continuing developing of an alternative fuels industry is the provision in the CAAA for the State of California, allowing the state to enact its own vehicle emissions-reduction program. Because of the severity of air pollution in its southern half, California has historically been in the forefront of emissions control technology development, evidenced by its initiation of lead-free gasoline and automobile catalyst systems. For alternative fuels, California's sophisticated and well-informed state agencies, the California Energy Commission, the California Air Resources Board (CARB), and the South Coast Air Quality Management District, have long been supporters of those fuels that can outperform conventional gasoline and diesel in terms of cost-effective emissions reduction.

In 1989, CARB formulated a set of increasingly stringent standards for low-emission automobiles, thereby creating several new classes of vehicles: transitional low-emission vehicles (TLEV), low-emission vehicles (LEV), ultralow-emission vehicles (ULEV), and zero-emission vehicles (ZEV). Sales of these vehicles are required to be phased in over the next 10 years so that an increasing fraction of California automobiles will be low-emission vehicles. Other states have the freedom to adopt the "California rules" in their entirety, and so far New

York State and other northeastern states have exercised this choice, with many other states considering joining.

The ability of alternative fuels, principally methanol and compressed natural gas (CNG), to compete against gasoline and diesel in the low-emissions stakes has been enhanced significantly by a further CARB rule that allows for the differing efficacy of exhaust pollutants in enhancing the rate of tropospheric ozone formation. Each fuel is awarded a "reactivity adjustment factor," which is used as a multiplier for the speciated main emissions. Because both methanol and CNG generate lower reactivity pollutants, they have an advantage over the more reactive components found in gasoline emissions.

In addition to the California rules, the federal government has derived its own set of regulations, generally less strict than California's. Further, sets of emissions performance criteria applying to medium- and heavy-duty vehicles have been drawn up. Tables 2 and 4 summarize the various rules, some of which are yet to be fully defined by the regulating entities.

In this situation, which represents the briefest of synopses of the current U.S. alternative transportation fuel regulatory environment, methanol as a fuel must compete against CNG (for fleets) and reformulated gasoline and diesel (for general use). It is therefore being required to prove itself in use against ever improving engine and emissions technology using conventional fuels before a market demand of significant volume has been built up, while withstanding the increasingly sophisticated scrutiny of the environmental movement.

Table 2 Passenger Car Emissions Levels: California and U.S. Federal Requirements

	Emission standards (g per mile)						
	CA TLEV	CA LEV	CA ULEV	CA ZEV	CAAA tier 1a	CAAA tier 2b	CAAA 1993
NMOG <sup>c</sup>	0.125	0.075	0.040	0			
NMHC <sup>d</sup>				0	0.25	0.125	0.41 <sup>e</sup>
CO	3.400	3.400	1.700	0	3.40	1.700	3.40
NO <sub>x</sub>	0.400	0.300	0.200	0	0.40	0.200	1.00
Formaldehyde	0.015	0.015	0.008	0			

a Effective 1994.

b Effective 2004 if adopted.

c Nonmethane organic gases.

d Nonmethane hydrocarbons.

e Total hydrocarbons.

Table 3 Implementation Rates for California Low-Emission Vehicles

Model year	% Fleet meeting NMOG emission standards				Fleet average standard (NMOG)
	% TLEV	% LEV	% ULEV	% ZEV <sup>a</sup>	
NMOG	0.125	0.075	0.040	0	
1994	10	0	0	0	0.250
1995	15	0	0	0	0.231
1996	20	0	0	0	0.225
1997		25	2	0	0.202
1998		48	2	2	0.157
1999		73	2	2	0.113
2000		96	2	2	0.073
2001		90	5	5	0.070
2002		85	10	5	0.068
2003		75	15	10	0.062

<sup>a</sup> The ZEV percentages are mandatory; other figures are indicative of acceptable averaging.

## 6.2

### Introduction

Although methanol has been used for decades to fuel automobiles, either neat or as an additive or extender to gasoline, its potential to fulfill the role of a commodity transportation fuel has only recently become a topic of significant commercial interest. As a chemically simple liquid fuel of reasonable cost derived independently of crude oil, it is being considered globally for a variety of fuel uses with the aim of generating benefits for the environment, energy security, or economics, depending on local circumstances. Among these uses are direct fuel applications in power generation, internal-combustion engines (e.g., substitution for conventional diesel or gasoline), and fuel cells, and indirect fuel use via such derivatives as methyl tert-butyl ether (MTBE), tert-amyl methyl ether, and methylated vegetable oils (biodiesel). This chapter is concerned only with direct fuel usage, but it should be noted that the rapid growth in demand for MTBE necessarily impacts the demand, supply, and price of fuel methanol.

Many countries have experimented with, and are continuing to assess, methanol's attributes in both direct and indirect fuel applications, but effort has been placed primarily on substituting methanol for gasoline and diesel. It hardly needs to be stressed that supplanting with methanol any significant fraction of the market demand for gasoline and diesel is a prospect being viewed with some misgivings by the oil industry and as a competitive opportunity by other, com-

Table 4 California Medium-Duty Diesel Engine Emission Level Requirements<sup>a</sup>

Vehicle weight (lb)	Emission standards (120,000 mile standards, g per mile)			
	NMOG	CO	NOx	PM
03750 1995+	0.360	5.0	0.55	0.08
LEV	0.180	5.0	0.60	0.08
ULEV	0.107	2.5	0.30	0.04
37515750 1995+	0.460	6.4	.098	0.10
LEV	0.230	6.4	1.00	0.10
ULEV	0.143	3.2	0.50	0.05
57518500 1995+	0.560	7.3	1.53	0.12
LEV	0.280	7.3	1.50	0.12
ULEV	0.167	3.7	0.80	0.06
850110,000 1995+	0.660	8.1	1.81	0.12
LEV	0.330	8.1	1.80	0.12
ULEV	0.197	4.1	0.90	0.06
10,00114,000 1995+	0.860	10.3	2.77	0.12
LEV	0.430	10.3	2.80	0.12
ULEV	0.257	5.2	1.40	0.06

<sup>a</sup> Beginning in 1998, a minimum percentage of all medium-duty vehicles will be required to be certified as low-emission vehicles according to the following schedule (year, % LEV, % ULEV): 1998, 25, 2; 1991, 50, 2; 2000, 75, 2; 2001, 95, 5; 2002, 90, 10; 2003, 85, 15. PM = particulate matter.

peting alternative fuels interests. Among the latter are ethanol and its derivative ethers, natural gas in the form of CNG or liquefied natural gas, and electrically powered vehicles of various types.

For the past few years, the manifold economic and environmental forces associated with the competitive situation just outlined have been interacting in the U.S. political arena, with the lead being taken by the State of California, principally because of the problems posed by poor air quality in Los Angeles. More recently, air quality improvement has been joined by energy security as a major driving force toward increasing utilization of alternative fuels in the United States, so the debate now encompasses not only the air quality benefits of methanol-fueled vehicles, but also the degree to which future methanol supplies may be sourced from countries external to the North American Free Trade Agreement. The future of fuel methanol is therefore being determined by some of the most powerful political and economic interests in the world, so it is not



surprising that market development has been extremely slow and difficult: most of these interests see methanol as a threat to be neutralized rather than an opportunity to be exploited. Inevitably, this high profile in turn has generated a large number of reports and vast amounts of data, of which this chapter is a brief summary.

As a chemical intermediate and solvent, highly pure synthetic methanol has been an article of commerce for several decades; its properties and distribution modes are familiar and well understood in this context. In the role of transportation fuel, however, considerations are so radically different that fuel methanol must be treated almost as a new product. This is so partly because the general public is exposed to contact when fueling vehicles and partly because engine combustion products and fuel distribution systems raise a host of new technological questions that have never been addressed by conventional chemical industry.

In the course of introducing this new fuel, major questions have therefore had to be addressed, among which education of the public in the face of competitive misinformation has been of key importance. Other major uncertainties have been the fuel-vehicle supply conundrum, the future price and source of fuel methanol, and the establishment of a fuel specification together with distribution infrastructure. During the 1980s and early 1990s, significant progress was made in all three areas. By mid-1993, with the advent of the Clinton Administration, the stage seems to be set for a rapid expansion of fuel methanol, spearheaded by federal fleets and proliferating to general use in light- and heavy-duty vehicles.

### 6.3

#### General Considerations

Ever since it became clear that the United States, led by California, was seriously determined to encourage the clean-burning alternative fuels, methanol has had to prove its acceptability as transportation fuel, not just while experiencing fierce opposition from the established conventional fuels but also while coping with competition from other aspirant industries seeking access to the same market opportunity. Thus methanol protagonists have had to present their case for methanol on a variety of fronts: political, legislative, economic, and technical while defending their product from the combined assaults of the oil companies, gas and electric utilities, and the ethanol industry (backed by the U.S. farm lobby). That methanol is still a major contender in the face of such formidable adversaries reinforces the conviction that the methanol case has very considerable merit.

The ensuing debates have been concentrated at two locations, Washington, D.C. and Sacramento, California, with satellite engagements in Austin, Texas

and Albany, New York. The consensus emerging from these debates is that no single fuel will emerge as an unequivocal winner in the near future, but rather that all the alternatives will find significant niches, either geographical (i.e., CNG vehicles in Texas) or technical (e.g., methanol flexibly fueled automobiles for general fleets). Among these contenders, the eventual major winner will be the fuel that can best satisfy the requirements of the private automobile while meeting all the goals of the legislature and the acceptability criteria set by the market-place. There are many reasons why the widespread fuel of choice will ultimately prove to be methanol.

## 6.4

### Fuel Supply Conundrum

A fundamental obstacle facing the introduction of any new consumer-oriented transportation fuel is the difficulty of providing simultaneously both a new alternatively fueled engine and widespread fueling infrastructure. Consequently, there exists a familiar stalemate: no cars are bought unless there is access to fuel to power them, and no fueling stations are built unless there is sufficient demand from vehicles using the fuel to justify the associated capital outlay.

It was the need to break this impasse that led officials in the State of California to propose and implement the flexibly fueled vehicle (FFV) strategy. This concept neatly bypasses the problem of fuel supply by making available a vehicle capable of being fueled with either gasoline or M85 (a mixture of pure methanol with 15% gasoline). This transition strategy therefore enables alternatively fueled vehicles to penetrate the marketplace by removing the obstacle of restricted fueling facilities in the early years. At the same time, the addition of 15% gasoline allows three other problems of methanol to be successfully dealt with, each of which stems from the low volatility and chemical simplicity of methanol.

First, cold starting is difficult with pure methanol fuel, partly because methanol lacks the highly volatile butane component of gasoline, which provides vapor to the cylinder even in very cold weather, and partly because methanol, like water, has a high heat of vaporization and thus quickly cools its surroundings when it evaporates. These effects make methanol a very efficient engine fuel but also make it difficult to start the engine without specifically engineered components not present in a regular gasoline engine. The addition of 15% gasoline provides sufficient vapor at low temperatures to enable FFV to start even in the coldest climates.

The second property concerns the potential explosivity of the vapor space in a partially empty fuel tank. Gasoline has such high volatility that except on the coldest days, the space above the fuel is too rich in vapor to be ignitable, whereas methanol vapor pressure leads to gas-phase composition within the ignitable

range. Fortunately, the problem is easily solved by addition of 15% gasoline; even with pure methanol, simple mechanical precautions have been developed that can avoid the problem altogether. In addition, the safety of methanol fuel tanks has been amply demonstrated by tests in which fuel tank explosions have been deliberately initiated by incendiary bullets, the only observable effect being a slight buckling of the tank [1].

Third, that methanol is a simple, pure chemical whose molecular formula involves no carbon-carbon bonds leads to its flame being virtually nonluminous. The luminosity of a flame normally stems from the formation at the flame surface of hot, glowing carbon particles, which can subsequently materialize on cooling in the form of smoke. Methanol, as a clean-burning fuel, does not form smoke and its flame is therefore nonluminous. This in turn can, ironically, cause a fire safety hazard in those circumstances in which methanol may be spilled and ignited without other flammable smoke-forming materials being present. Addition of smoke-generating gasoline provides sufficient flame luminosity for acceptability as a fuel for FFV while measures to avoid the luminosity problem are being sought for application to pure methanol fuel [2].

Following the introduction of the M85 concept, flexibly fueled vehicles have been made available by all the major car manufacturers, including General Motors, Chrysler, Ford, Volvo, Mercedes, Volkswagen, and the Japanese majors: there were nearly 10,000 such vehicles in operation in California by mid-1993. However, it is important to bear in mind that the FFV is essentially a compromise and does not therefore offer the best performance achievable in terms of either emissions or fuel economy. Thus, although FFV represent a powerful means of circumventing the fuel supply conundrum, they also possess a fundamental weakness that competitive fuel suppliers, particularly the oil companies, have been quick to exploit. An optimized gasoline engine operating on the "cleanest" reformulated gasoline can approach the emissions performance of a compromise FFV operating on an M85 fuel whose gasoline component may contain more than 65% aromatics [3]. That FFV represent merely a transition to the extremely low emissions that an optimized dedicated M85 vehicle will offer can readily be lost under such circumstances.

## 6.5 Acceptability

Analysis shows that there are six basic areas having sets of criteria that must be fully met before a given fuel can be considered acceptable for general use by society. For example, the go-anywhere, unrestricted car user will suffer no lessening of driving freedom, a consideration that places limits on minimum driving range and fuel storage and availability in remote locations. In time, such



Figure 1  
Six criteria for alternative fuel acceptability.

matters determine boundary limits of fuel projects. The six critical areas referred to are listed in Figure 1.

To gain general acceptance, it is necessary for any alternative fuel to withstand scrutiny with respect to each of the critical areas. In this chapter, we discuss the advantages and disadvantages that methanol offers: space precludes presenting a detailed comparison between methanol and the various other alternative fuels that are candidates for general transportation use.

### 6.5.1 Safety

The chief issues facing fuel methanol in the field of safety involve fire properties and human toxicity, each of which are prime concerns when the general public is exposed to fuel handling. Fortunately, a considerable amount of work has been performed on both topics, with the broad conclusion that methanol is safer than gasoline but less safe than diesel.

In terms of human toxicity, it is fortunate that most car owners are very familiar with the blue windshield washing fluid sold in 1 gal containers by service stations and stores throughout the United States, since the fluid formulation comprises between 50 and 70% pure methanol. This alone means that many consumer handling fears can be readily allayed: practically every car and garage contains methanol, and there are no associated problems generally experienced with skin contact, spills, exposure to vapor, or reports of adverse effects upon car paintwork.

Following the theme of public exposure, methanol's wide availability via such uses as fuel deicing fluid, antifreeze, and solvent applicationseven such domestic uses as fuel for chemistry sets and heaters for fondue cooking vesselsimplies that although public safety always requires vigilance, methanol poses minimal risk to the consumer.

The human body is of course the main focus for safety, and the ability of methanol to produce symptoms of toxicity following internal consumption has been widely discussed. Methanol is commonly encountered in the biosphere, and since it is frequently present in low levels in many beverages, the human body clearly has the capacity to metabolize small amounts of methanol without ill effects. Larger quantities of methanol can be toxic because, unfortunately, the immediate metabolic product of methanol digestion is formic acid, which hu-

mans (although not most other mammals) are slow to metabolize. Formic acid at high levels can give rise to acidosis (low blood pH), which can lead to deterioration of acid-sensitive tissue, particularly the optic nerve. Thus reports of blindness, usually temporary, often accompany cases in which large quantities of methanol have been ingested without antidote treatment. Reliable data are few, but most estimates, usually anecdotal, place a fatal dose at 23 oz. Cases are on record of survival following ingestion of more than 1 pint and fatality after 1 oz: thus sensitivity may be variable.

In response to the need to avoid accidental ingestion, the methanol industry proposes to add a small quantity of MTBE to fuel methanol as a taste and odor additive. In addition, to avoid accidental misidentification with water, a blue dye will be added. Between them, these measures should deter all but the most enthusiastic of would-be imbibers.

The Health Effects Institute, in its study of methanol, investigated liquid absorption through the skin and vapor absorption through the lungs [4]. It concluded that methanol's overall rate of absorption was significantly lower than the rate of its metabolism, even in a worst-case, real-life scenario. This important finding implies methanol can be used safely at fueling stations even by untrained personnel with minimal personal risk.

Because methanol is already a natural constituent of the ecosphere, low background exposure is a de facto reality for everyone. Accordingly, chronic subacute toxicity should not be a substantive issue, even though the Environmental Protection Agency (EPA) is planning a program for its investigation. By toxin standards, methanol of course possesses a very low toxicity. Figure 2 illustrates graphically a comparison of various well-known substances with some of the more lethal toxins known to science. It is the need to demonstrate that the commonplace hazards of fuel handling are reasonably acceptable for the general population that drives the continuing study of fuel methanol safety.

Where fire safety is concerned, the properties of methanol have been carefully analyzed by officials of the EPA, and compared with the corresponding fire hazard posed by gasoline [5]. A summary of the EPA conclusions derived from this study is that widespread use of pure methanol would result in a 90% reduction in the number of vehicle fires compared with gasoline, and the M85 blend would yield a 45% reduction. To support this conclusion by practical demonstration, the EPA and the Southwest Research Institute have filmed typical car fires involving gasoline and methanol. In one dramatic test, two cars, one fueled with methanol and one with gasoline, were allowed to leak fuel at equal rates onto the ground adjacent to an open flame. The gasoline leak ignited quickly and the resulting fire consumed the entire vehicle within minutes. The spilled

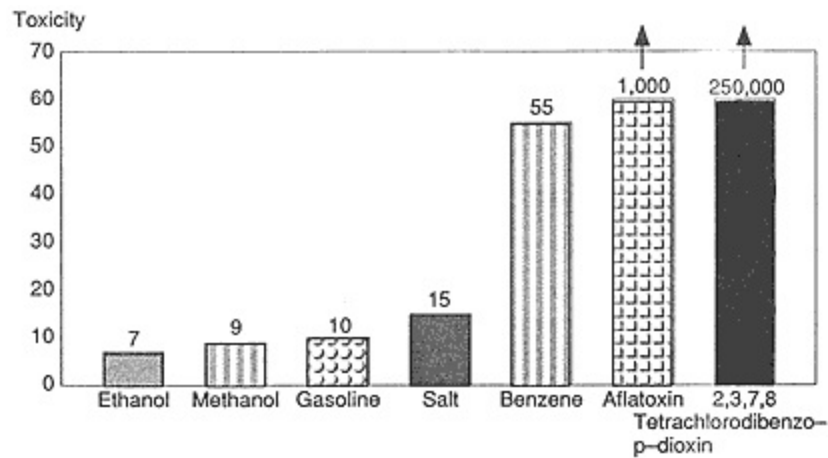


Figure 2

Comparative mammalian toxicity chart. Toxicity is represented by the number of oral doses lethal to a typical 1 kg mammal per 100 g (approximately 3.5 oz) of the named substance.

methanol took three times longer to ignite, and the resulting fire damaged only the rear half of the vehicle.

The main properties underlying the reduced fire hazard are the low volatility of methanol and its low-temperature, smokeless flame, as described earlier. A very important, although not obvious safety advantage possessed by methanol arises because the methanol flame possesses a low radiant heat output, which is a direct consequence of its smokelessness and low luminosity. This is a significant benefit, because not only does it allow a closer approach by fire fighters but also there is a much lower probability of fire spreading to nearby ignitable materials, and it is therefore much easier to put the fire out.

To underpin the EPA conclusions, Indianapolis racing cars have been using solely methanol fuel for the last 25 years or so, without significant mishap. Indeed, the main reason for switching from gasoline to methanol was safety: methanol's low smoke production gives high visibility on the track so that in the event of a fire, following vehicles can take safe evasive action.

In summary, the difficulty of ignition, low-temperature flame, low radiant heat output, and ease of extinguishing together mean that compared with gasoline, methanol fires are less likely to occur and less damaging when they do occur.

Finally, formaldehyde emissions are frequently raised as an issue of particular environmental importance for methanol vehicles on two counts: first, there is concern for formaldehyde as an air toxic, and second, there is its role as a highly reactive ozone precursor. Formaldehyde is a gas that is naturally present at low concentrations in the atmosphere, originating as an intermediate in the slow photooxidation of various organic compounds released into the environment from a variety of sources. As a low-level constituent of engine exhaust, it is also emitted directly into the air by both diesel and gasoline vehicles.

Early versions of methanol-powered automobiles and heavy-duty engines tended to suffer from noticeably odorous formaldehyde emissions. The same odor is prevalent at Indianapolis 500 races. Formaldehyde is a product of the incomplete combustion of any carbon-based fuel, so poorly designed engine systems or lack of catalytic controls can give rise to readily detectable emissions, particularly when the engines are cold. The human nose can detect extremely low concentrations of formaldehyde, which is sensed as acrid and unpleasant.

For these reasons, CARB early placed tight limits on formaldehyde emissions from methanol-fueled engines. Fortunately, the high reactivity of formaldehyde means that it is readily removed by catalytic oxidation, so that the limits can be attained by careful control of combustion parameters and catalyst system designs.

Like methanol itself, that low levels of formaldehyde are normal and natural constituents of the biosphere tends to defuse genuine concerns about longterm exposure. Even so, because formaldehyde has been classified as a probable human carcinogen by the EPA (largely because a specific strain of rats suffered from nasal carcinomas when exposed to very high concentrations), there is continuing attention addressed to this topic.

## 6.5.2 Energy Security

Most industrialized nations are vulnerable to changes in the availability of imported energy since the efficient functioning of their economies, as well as their defense equipment in the event of war, depends largely on access to a reliable fuel supply. As the world's predominant energy user, the United States is particularly sensitive to this issue. The Gulf War and EPACT are recent examples illustrating the gravity with which U.S. dependence on foreign oil is viewed by congress and the extreme measures deemed necessary to achieve energy security in a situation in which oil is cheap, in surplus, and available globally.

The U.S. Department of Energy early realized that with the eventual depletion of crude oil reserves the long-term energy requirements of the United States could be met only by coal, tar sands, and oil shale, provided fusion and other forms of nonfossil energy prove to be unviable. In the medium term, domestic fuel needs can be met by natural gas since current estimates of total reserves





exceed 50 years, considerably longer if Canada's natural gas reserves are included. The only fuel that can be made from all these domestic resources, that can be stored and transported as a liquid, and that can be utilized in power stations, diesel engines, and gasoline engines is methanol (Fig. 3).

Some opponents of methanol claim that it should not be considered a domestic fuel since future expansion of manufacturing facilities will occur overseas, where very low cost gas is available. So far, this argument has been without merit. Incremental methanol production has continued to be placed in the United States, largely because lower capital costs, easier capital availability, shorter construction time, political stability, and access to the largest world market have tended to outweigh the benefits of cheaper gas. There is an opposing argument, which holds that provided the infrastructure and technology are in place to use methanol, it is preferable to import it in the short term (so long as it is low cost), thereby to preserve domestic reserves of gas for use over a longer time period. This view has been overshadowed by the attractions of maximizing domestic production to generate short-term economic benefits and preserve both jobs and business competitiveness.

Energy security can also be enhanced through energy diversity: fuels that avoid oil, such as nonassociated natural gas used as a feedstock for methanol, can either reduce dependence on or avoid altogether the "conventional" crude oil-producing countries. In this way, even methanol produced overseas would still contribute a measure of security to those countries that import energy since it would lessen their dependence on the Organization of Oil-Exporting Countries (OPEC). Gas is very widely distributed throughout the globe, minimizing the likelihood that a gas cartel similar in nature to OPEC would form. For example, Tables 5, 6, and 7 show reserves and economics of nonassociated gas totaling 3849 trillion cubic feet (tcf) for selected countries. The countries constituting the former Union of Soviet Socialist Republics alone own 809 tcf exportable gas. These figures should be viewed against a total current U.S. natu-

	Feedstocks	Fuel Outlets
Fossil	Regenerable	Power Stations
Coal, Lignite, Peat	Biomass	Diesel Engines
Natural Gas	Landfill gas	Gasoline engines
Associated Natural Gas	Sludge	Fuel Cells
Oil Shale	Agricultural Wastes	Turbines
Tar Sands	Cellulosic Garbage	Heat Engines
Crude Oil	Vegetable Oils	
Biomass		

Figure 3  
Potential feedstock sources and market applications of methanol.

Table 5 Economically Recoverable Natural Gas Reserves of Selected Countries

Origin	Proven reserves (tcf)	Exportable surplus (tcf)
Former USSR	1450	809
Iran	489	158
USA	187	0
Abu Dhabi	184	155
Qatar	157	152
Saudi Arabia	140	0
Algeria	106	40
Canada	95	12
Venezuela	95	14
Norway	89	56
Nigeria	84	67
Australia	79	53
Mexico	76	0
Indonesia	73	46
Netherlands	64	10
Malaysia	52	29
Other Middle East	122	0
Other Asia Pacific	113	25
Other Europe	77	3
Other Latin America	61	31
Other Africa	56	6
Total world	3849	1666

Source: From Reference 17.

ral gas annual usage of approximately 20 tcf. It should also be noted that exploration for new gas fields is not of great concern outside the industrial nations simply because there are more than ample supplies to meet existing demand. Thus methanol, as an effective way of transforming natural gas into a transportable and storable liquid, offers long-term availability, security, and diversity whether derived from domestic or foreign sources.

### 6.5.3

#### Environment

All alternative fuels contending for widespread application in the transportation sector must satisfy criteria for environmental acceptability on a "cradle-to-grave" basis: that is, the environmental impact of all the steps involved in the process

Table 6 Methanol U.S. East Coast Landed Price (Gas at \$1/mcf)

Origin	Current technology (¢/U.S. gal)	Advanced technology (¢/U.S. gal)	No. world-scale methanol plants supportable at \$1/mcf
Trinidad	41.4	29.4	8
Venezuela	41.4	29.4	6
Algeria	42.9	30.9	60
Libya	42.9	36.9	14
West Russia	52.9	38.9	36
Chile	54.1	40.1	23
Argentina	54.1	40.1	28
Middle East	56.5	42.5	2104
Nigeria	67.5	47.5	40

Source: From Reference 18.

Table 7 Methanol U.S. West Coast Landed Price (Gas at \$1/mcf)

Origin	Current technology (¢/U.S. gal)	Advanced technology (¢/U.S. gal)	No. world-scale methanol plants supportable at \$1/mcf
Indonesia	46.9	34.9	57
East Russia	51.9	37.9	3
Australia	54.9	40.9	17
Malaysia	54.9	40.9	24

Source: From Reference 18.

of using the fuel, from production of the feedstock to utilization of its energy in an engine, must be evaluated. Figure 4 illustrates the overall process for methanol.

Fortunately, the environmental risks involved in methanol production and exploitation are relatively small, largely as a consequence of its high volatility, water miscibility and metabolizability. For example, much of the environmental hazard and cost of handling crude oil and its derivative fuels arise from their very low water solubility, so that even minor spills can cover the water surface over a very large area, and their low-volatility components ensure that the ef-

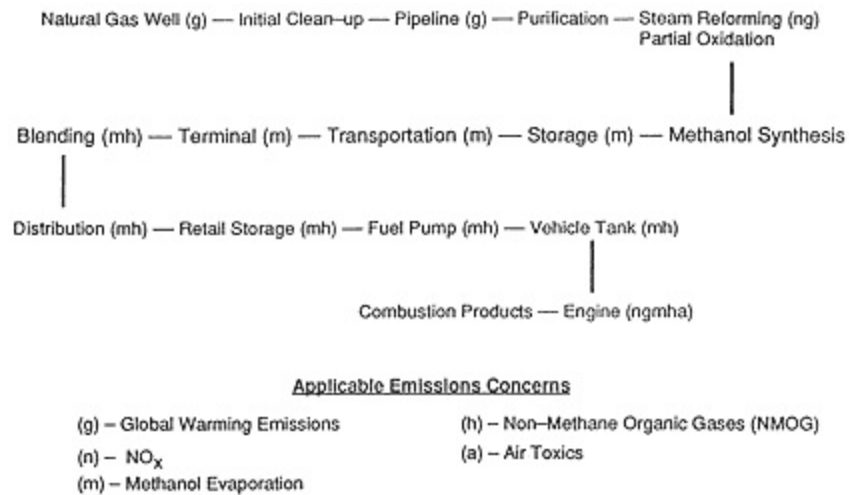


Figure 4  
Fuel methanol life cycle environmental considerations.

fects of any oil spillage linger over a longer time period. In contrast to oil, methanol rapidly becomes diluted by local water in most spillage situations to the point at which it is readily metabolized by ambient organisms.

A methanol plant is typically sited near a gas field, so that leakage of natural gas from an extensive network of old pipes is not a problem. (Methane, the major constituent of natural gas, is a highly effective global warming gas, and leakage from aging distribution systems has been pinpointed as a significant source of incremental anthropogenic global warming [6].) However, since natural gas is frequently associated with carbon dioxide, which must be separated and vented into the atmosphere, methanol production involves a measure of avoidable global warming. It should also be noted that 1015% carbon dioxide is often added to the synthesis gas mixture in the methanol synthesis loop to maximize feedstock efficiency, so that at least some of the release of global warming potential is mitigated via carbon dioxide conversion.

In general, leaks, spillages, and emissions from methanol plants are minor, and marine, estuarine, and fluvial spillages are relatively benign compared with those of oil products. In fact, cases are on record in which methanol could not be detected following riverine spillage because dilution to undetectable limits is so swift. Calculation shows that even a massive marine supertanker incident would have minimal environmental impact: instantaneous release of 100,000 ton

(300 million gal) methanol into the sea, for example, would typically result in a concentration of less than 0.1% within a 1 mile radius, at which point methanol is readily assimilated by marine life. The net ecological affect of such an incident would be close to zero, in contrast to the disaster that would occur if equivalent volumes of crude oil were involved.

The major environmental hazard connected with fuel methanol is uncertainty concerning the fate of the 15% gasoline component of M85 when aquifers may be potentially contaminated via service station tank leaks or tank truck collision spillages. Little data exist, since there is no experience with major M85 leaks. New service station methanol tanks are required to be double-walled, a requirement that should limit the hazard. Nevertheless, ongoing work to define the extent of the potential hazard concerning gasoline transport via M85 is being undertaken by the EPA. Since aromatics have a finite solubility in water (benzene is soluble in water  $\sim 0.08\%$  at ambient temperatures), the problem is already a real factor in aquifer pollution by gasoline, which typically contains 0.52.0% benzene and 1030% aromatics. General substitution of gasoline by M85 would therefore reduce aromatics pollution by a factor of 67, assuming the 15% gasoline component of M85 has the same composition as regular gasoline and that M85 would suffer the same leakage rate hazard as gasoline.

#### 6.5.4 Economics

It is an ironic fact of life that the more remote a given technology is from real-life application, the less emphasis is placed on economic viability and the more resources it seems able to command. Thus research into fuel cells and advanced batteries receives very large grants from government sources, whereas methanol engine development has received very little. On the other hand, methanol has been the subject of detailed scrutiny of every aspect of its economics in a multitude of reports sponsored by a variety of organizations. These include, in the United States, state and federal agencies, private industry, research foundations, and universities. Against the real-life feasibility yardstick, methanol must be very close to general acceptance. However, if methanol is to supplant a significant fraction of the gasoline and diesel fuel currently used, it is appropriate that economic considerations should be emphasized, although they should not be paramount. Assessment of new technologies is notoriously difficult, particularly for alternative fuels, because not only is a cost-benefit analysis required for air quality and energy security effects based on today's knowledge, but it is also necessary to take a view on the capacity for the future development of engine performance and fuel distribution technologies. How many people foresaw traffic signals and underpasses when the internal-combustion engine was invented? In

these circumstances, careful comparison of fundamental qualities must be made in the context of utilitarian and economic criteria. Unfortunately, such comparisons are frequently skewed in the economic arena because there is a lack of equity in society's treatment of the competing fuels on the so-called level playing field. Transportation fuel economics should take into account five major areas of financial concern: the cost of fuel production, the costs of distribution and storage (infrastructure), the incremental cost of associated engine and emission technologies, the nature and extent of local, state, and federal taxes, and the potential for and quantification of emissions reduction credits, as well as benefits accruing to society from reduction in the indirect environmental costs associated with conventional fuel use. Each of these areas has been acknowledged and discussed in the public arena without any consensus emerging, largely because no dedicated fuel methanol plant and distribution system is yet in existence to test basic assumptions. In practice, demand is being satisfied using conventional chemical methanol infrastructure, but the potential size of the market is so large (Table 8) that future distribution systems will have to be modeled on current gasoline practice. Similarly, engine assembly plants are not designed solely to produce methanol vehicles, with the result that the benefits of mass production have not thus far been applicable [7].

#### 6.5.4.1

##### Cost of Methanol Fuel Production

Chapter 3 in this book deals with the production of chemical methanol, from which the basic economics of fuel methanol production differ but little. Most sources of cost, such as provision of gas feedstock, purification systems, gasification, synthesis, and distillation, remain broadly the same in the context of fuel: only distillation limits can be relaxed slightly, a measure yielding small economic benefit. The prospect of fuel, however, lends some new perspectives on methanol production. For example, fuel involves a market of much higher volume than chemical methanol, so considerations of energy security and longer term gas supplies arise. In particular, fuel allows much larger facilities to be constructed, resulting in prospects for significant cost reductions. Many fuel methanol studies have evolved around a conceptual fuel complex of four 2500 t per day methanol synthesis units operated cooperatively at one site. Such studies are important because they facilitate estimates of realistic methanol prices at a time in the future when a large-scale demand will exist. To apply current chemical methanol prices in a situation in which demand is minimal is clearly misleading, especially when opposition fuels already enjoy the benefits of a national fuel distribution infrastructure funded and maintained by utility-financing mechanisms. Most such studies forecast bulk fuel methanol prices around 30–35¢ per U.S. gallon [8]. Current quotations hover around 45¢ per U.S. gallon, and chem-

Table 8 Potential Market Size of Fuel Methanol in the United States

% Total transport-fuel penetration by methanol	Methanol volume demand per year (Mt) (billion U.S. gal)		No. world-scale plants required (2500 tpd)	Natural gas usage per year (tcf)
Current world methanol production	20	6.7	25	0.6
10	50	17	62	1.5
25	125	42.5	155	3.7
50	250	85	310	7.4
100	500	170	620	15

ical methanol has varied in recent years between 26¢ and 70¢ per U.S. gallon. At its lowest price, methanol could therefore compete easily with regular gasoline prices in the United States and could come close to meeting bulk diesel prices, provided that other factors, such as taxation, are equitably applied.

6.5.4.2  
Distribution and Storage

Compared with chemical methanol, the cost of shipping fuel methanol by sea should be significantly lower for two reasons. The first is that the exceptionally high purity required of chemical methanol necessitates costly delays while tankers are cleaned and inspected, and further expenses are associated with provision of dedicated tankers, analyses, and insurance. All these can be largely avoided since the fuel methanol specification allows considerably more latitude in impurity content. Second, because fuel methanol will be delivered in bulk to relatively few customers, supertankers can be used: there is no reason that methanol should cost more per gallon to ship than any other liquid shipped in comparable volumes. Thus the ultimate cost of shipping methanol should be the same as crude oil, ~4¢ per gallon.

The other means of transporting large volumes of liquid is via pipelines, a method that offers very significant benefits over road or rail transport. Despite frequent assertions that methanol pipelining would not be practicable, methanol has been very successfully transferred by pipeline in two demonstrations conducted in Canada in 1986. One demonstration involved a crude oil line running from Edmonton, Alberta to Burnaby, British Columbia, a distance of 716 miles; the other used a liquefied petroleum gas pipeline over a distance of 1819 miles. Figure 5 shows analyses of the two shipments, each of which comprised 4000 t. In both cases, the transfer was effected well within the impurity limits dictated by any proposed fuel methanol specification. Such pipelined distribution of methanol must become standard if a significant fraction of the current transportation fuel market is gained by fuel methanol (see Table 5).

Via Trans Mountain Crude Oil Pipeline		
	Leaving Edmonton, Alberta	Arriving Burnaby, British Columbia
Methanol Content %	99.99	99.68
Hydrocarbon Content %	0	0.29
Water Content %	0.01	0.02
Nonvolatiles %	0	0.01

Figure 5  
Pipelined methanol feasibility demonstration: Edmonton to Burnaby.  
(From Ref. 12.)



### 6.5.4.3

#### Incremental Vehicle Costs

Estimates of the true incremental costs of manufacturing an automobile designed to run on methanol presents some difficulty because the relevant facts are not readily available from the automobile industry [7]. Nonetheless, since methanol is a liquid similar to gasoline, methanol automobile-manufacturing processes are more or less conventional, and the mass-produced cost of a methanol vehicle should be little different from the cost of producing a gasoline vehicle of the same emissions category. Minor differences can arise. For example, fuel tanks need to be double normal capacity for methanol to achieve the same range as gasoline. Similarly, FFV need fuel sensors and associated circuitry for providing variable fuel capability (see Fig. 6). On the other hand, the emissions reduction hardware can be less sophisticated for methanol vehicles because catalysts are required to deal with a smaller range of pollutants and the sulfur-free nature of methanol implies that less stress is placed on the catalyst. (Sulfur is present in gasoline, and sulfur-containing exhaust gases reduce significantly both the activity and the useful life of emissions reduction catalysts. The 1990 Clean Air Act mandates further reduction in sulfur level in gasoline.)

### 6.5.4.4

#### Taxation

Taxation is the "loose cannon" on the alternative fuels playing field in that it can be used arbitrarily as a powerful and decisive influence on the outcome of cost comparisons made by potential fuel users. Heavy negative taxation (e.g., subsidy) of fuel ethanol in the United States, for example, has kept that fuel alive when a competitive marketplace would have rejected it long ago.

In 1993, fuel tax policy was being seriously debated by congress and a final outcome has not yet been realized. A straightforward new tax on energy content has been rejected, and instead, there has been proposed a volume-based tax that extends existing tax law. Unfortunately, all the alternative fuels possess lower energy per unit volume than gasoline or diesel, so the new extension tax disadvantages the very fuels congress has itself decided to encourage in EPACT. At the same time, most states place widely varying taxes on methanol, CNG, and gasoline. To compound the complexities, CNG is not required to pay the federal highway tax of <sup>14¢</sup> per gallon gasoline equivalent that applies to all the nongaseous fuels. Table 9 illustrates the resulting tax inequities by comparing the differentials in taxation in various states of the United States [9].

The Presidential Task Force on Alternative Fuels recommended that alternative fuels taxes should either be removed or drastically lowered. At the time of writing, this recommendation appears to have been more than ingored: gasoline is actually receiving fiscal encouragement. Resolution of these inequities awaits the harmonization of the U.S. administration's fiscal policy with its environmental policy, a process that may take

considerable time.

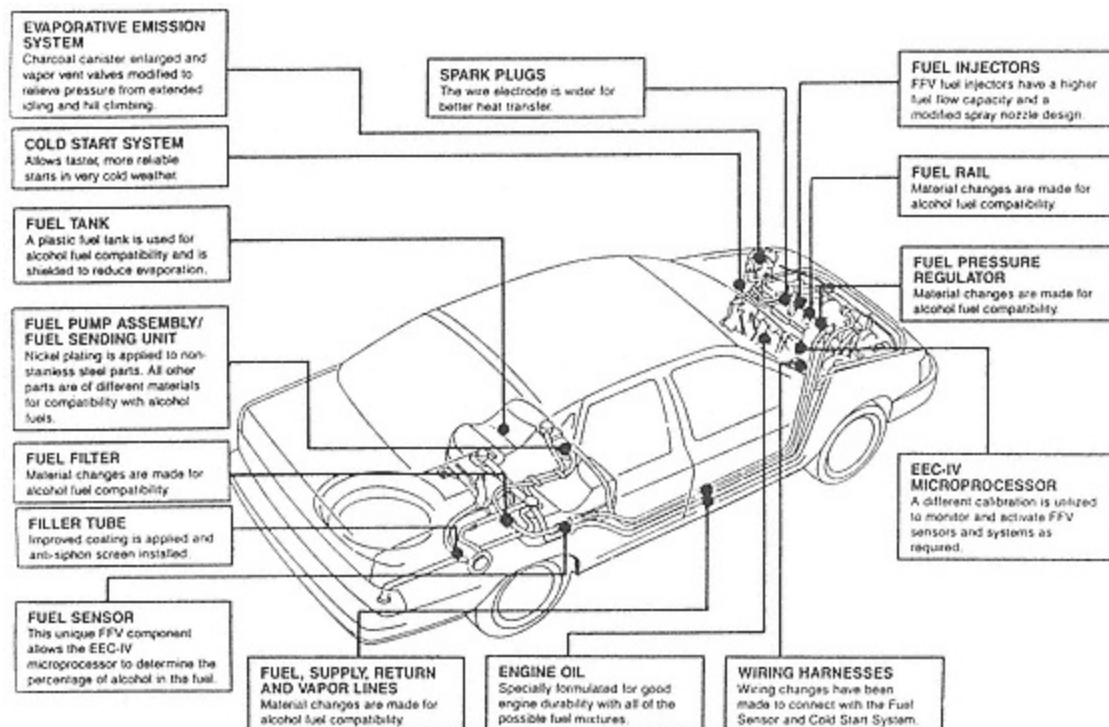


Figure 6  
Unique 3.0 liter Ford Taurus FFV components.

Table 9 Total Taxes (State and Federal) on Methanol, CNG, and Gasoline in Selected States

State	Methanol (¢/U.S. gal equivalent)	a CNG (¢/U.S. gal equivalent)	Gasoline (¢/U.S. gal)
Arkansas	50.8	0	37.0
Arizona	49.2	1	36.0
California	29.7	7	34.9
Connecticut	68.8	28	47.1
Florida	37.3	12	29.2
Georgia	29.5	7	24.8
Illinois	51.2	19	35.1
Louisiana	53.2	20	38.2
Massachusetts	55.2	21	39.3
New Jersey	35.3	5	28.1
New York	29.7	8	41.6
Ohio	55.2	21	39.3
Pennsylvania	37.4	12	34.4
Texas	53.2	20	38.2
District of Columbia	53.2	20	38.2

a Energy efficiencies assumed equal. In practice, methanol is approximately 12% more efficient than gasoline, resulting in slightly low effective tax rates per mile.

Source: From Reference 9.

## 6.6

### Methanol as a Fuel

Many properties of methanol are of little importance to its chemical applications but can be critical to its success as a fuel. Table 10 lists a variety of physico-chemical parameters that must be considered in the context of transportation fuel. Broadly, such considerations center around engine technology, fuel handling, and human exposure risk.

In some areas, methanol lacks a characteristic required of a fuel. For example, as previously discussed, methanol burns with a virtually nonluminous flame, constituting a hazard that may need to be addressed with an additive. In other areas, methanol suffers drawbacks because of its incompatibility with gasoline.

From the chemical viewpoint, methanol is a simple small molecule completely miscible with water. It has a high dipole moment and high dielectric constant and is associated in its liquid state. It is therefore a good solvent for ionizable substances, such as acids and salts, as well as for certain plastics. Gasoline, on

Table 10 Methanol Fuel Parameters (see also Specification, Fig. 7)

Formula	CH <sub>3</sub> OH
Molecular weight	32.04
Density at 60°F, 1 atm	49.6 lb/ft <sup>3</sup> 6.63 lb/gal 0.796 g/ml
Boiling point	148.2°F
Freezing point	143.3°F
Vapor pressure, psi at 100°F	4.63
Latent heat of evaporation	3070 Btu/U.S. gal
Gross heating value	64,767 Btu/U.S. gal
Net heating value	57,070 Btu/U.S. gal
Autoignition temperature	~800°F
Adiabatic flame temperature	3,400°F
Stoichiometric flame speed	1.4 ft.s
Electrical conductivity at 46°F	$4.4 \times 10^7$ S/cm
Vapor density versus air	1.11
Flash point	52°F
Flammability limits	6.736.5 vol%
Stoichiometric air-fuel ratio	6.46 mass 7.15 vol
Sulfur content	0
Dielectric constant at 68°F	33.58
Diffusivity in water	$1.6 \text{ cm}^2/\text{s} \times 10^5$
Specific heat at 20°C	0.6 cal/g
Viscosity, cP at 60°F	0.64
Research octane number	106
Motor octane number	92

the other hand, is a complex mixture of many different kinds of hydrocarbons, the vast majority of which have zero dipole moment, low dielectric constant, and no miscibility with water and are nonassociated as liquids. Thus gasoline is a good solvent for unpolarized covalent materials and is completely different from methanol. Unfortunately, in its fuel applications, methanol is required to fit into a marketplace and a technology in which expectations and experience are predicated on gasoline. It is this feature that has led to various charges that methanol is corrosive and threatens the integrity of materials. The plastics, rubbers, and metals used in the process of storing, pumping, and delivering gasoline will be predictably often incompatible with methanol: the reverse would of course be true.

## 6.6.1

### Engine Technology

Compared with direct corrosion and chemical attack, a more subtle incompatibility arises with lubricating oils. Since gasoline and diesel are derived directly from crude petroleum, it was natural that early pioneers would turn to the lower boiling fraction of crude oil to provide lubricating oils and greases for the engines powered by the fuels. Questions of compatibility did not arise simply because both fuel and lubricants shared the same chemical characteristics. In contradistinction, methanol presents problems because it is incompatible with the lubricant systems designed for gasoline and diesel engines. Ideally, synthetic oils must be developed with chemical kinship to methanol. Such oils are known and, in some cases, are being marketed. Although not yet perfected, they offer in the long term an opportunity for methanol engines to demonstrate longevity and durability equal to or surpassing those of the corresponding conventionally fueled engines. In the meantime, methanol fuel use is handicapped by the need to compromise, particularly with FFV, between the very different lubrication needs of gasoline and methanol.

In addition to the basic incompatibility of lube oil stock, a further problem arises with additive packages. Most lubricant oils, especially those used in high-performance engines, contain several additives designed to confer specific properties on the oil to improve, maintain, or measure their performance. These can include dyes, buffers, antioxidants, detergents, antifoamers, and emulsifiers, depending on the application. Such packages have evolved over the years so that each individual additive is compatible not only with the lube base but also with its fellow additives and with competitors' products. It would be unacceptable, for example, if it were impossible to mix one lube oil product with another when refilling or replacing engine oil. Since all crude oil lubes are chemically similar, compatibility has hitherto been no problem. The advent of fuel methanol raises some difficulty because, for optimal performance, new lubes and additives need to be devised. Thus there arises another example of the supply-production conundrum: optimized lubricant and additive packages for methanol vehicles will not be developed unless or until there is a sufficiently large demand to justify the expense of development, but such a demand may not occur if the engine performance proves unsatisfactory without optimized lubricants.

This problem is most clearly exposed with FFV because it is inevitable that M85 and regular gasoline, each with its packages, will become commingled in the fuel tank. Already some difficulties have been experienced with filter plugging because of this factor. So far it has been possible to design around the problem, but in the longer term, optimized lube and additive packages developed specifically for methanol fueled engines will become necessary if the full potential of methanol to improve engine performance is to be realized.

## 6.6.2

### Fuel Handling

For technical and legal reasons, a fuel must be closely defined by a specification before it can become widely available. Thus far, the American Society for Testing Materials (ASTM) has considered specifications for M85 and M100 without reaching a final recommendation. CARB has issued specifications that are given in full in Tables 11 and 12 and which may eventually form the basis for a national or even international consensus. It is significant that the CARB specification requires the 15% gasoline component of M85 to be reformulated (i.e., low sulfur, aromatics, and olefins), whereas most testing of M85 emissions performance has been conducted with 15% regular gasoline containing up to 66% aromatics [3]. Needless to say, the results of such testing show lower emission benefits than would have been obtained with reformulated gasoline.

The major problems experienced to this point with methanol fuel handling have revolved around M100 flame luminosity, corrosion of aluminum and its alloys in fuel systems, and the lube oil and additive incompatibility just described. However, a variety of other considerations must be addressed. For example, excess water in methanol can enhance diesel engine deposits, ionic impurities can adversely affect conductivity devices designed to measure methanol-gasoline ratios, and high ash content can give rise to valve problems. In general, solutions have been found to these and other concerns, which are typical of the teething troubles encountered when new technology is grafted onto old.

## 6.6.3

### Fuel Additives

Pure methanol, like water, is a clear, colorless, transparent, highly mobile fluid with little odor or taste. The risk of confusion with water is therefore real and must be minimized to acceptably low levels before public exposure can be promoted. Appropriate additives providing color (blue), taste, and odor have been identified but have yet to receive official recognition.

In general, additives for methanol can be classified into two categories, generic and proprietary, according to whether the property desired to be modified is a fuel property that differentiates methanol as a fuel product (generic) or is designed to promote specific behavior in an engine system, such as detergency (proprietary). Table 13 lists the critical factors in determining whether a given additive will be satisfactory, the most difficult to determine being, of course, compatibility with other additives.

In the latter category fall ignition-improving additives. These, like cetane improvers used in diesel fuel, enable methanol to ignite readily in diesel engines and, therefore, open up the diesel market to methanol without the need to use the electrical ignition systems that would otherwise be necessary. They also

Table 11 California Air Resources Board M85 Fuel Methanol Specification

Specification	Value	Test method
Methanol + higher alcohols	84 vol% (min)	Annex A1 to the ASTM D-2 Proposal P-232, Draft 8-9-91
Higher alcohols (C2C8)	2 vol% (max)	ASTM D4815-89
Hydrocarbons + aliphatic ethers <sup>a</sup>	1316 vol%	ASTM D4815-89, and then subtract concentration of alcohols, ethers, and water from 100 to percentage hydrocarbons
Vapor pressure, dry <sup>b</sup>		Methods contained in Title 13, Section 2262 must be used. ASTM D-4953-90 is an alternative however, in case of dispute about the vapor pressure, the value determined by the methods contained in Title 13, Section 2262 shall prevail over the value calculated by ASTM D4953-90, its precision statement
Luminosity		Shall produce a luminous flame, which is visible under maximum daylight conditions throughout entire burn duration
Acidity as acetic acid	0.005 mass% (max)	ASTM D1613086
Total chlorine as chloride	0.0002 mass% (max)	ASTM D3120-87 modified for determining organic chlorides, and ASTM D2988-86
Lead	2 mg/L (max) <sup>c</sup>	ASTM D3229-88
Phosphorus	0.2 mg/L (max) <sup>d</sup>	ASTM D3231-88
Sulfur	0.004 mass% (max)	ASTM D2622-87
Gum, heptane washed	5 mg/100 ml (max)	ASTM D381-86
Total particulates	0.6 mg/L (max)	ASTM D2276-89, modified to replace cellulose acetate filter with a 0.8 µm pore size membran
Water	0.5 mass% (max)	ASTM E203-75
Appearance	Free of turbidity, suspended matter, and sediment	Visually determined at 25°C by Proc. A of ASTM D4176-86

<sup>a</sup> Hydrocarbon fraction shall have a final maximum boiling point of 225°C by ASTM method D86-90, oxidation stability of 24 ASTM test methanol D525-88, and No. 1 maximum copper strip corrosion by ASTM method D130-88. Ethers must be aliphatic and manganese added. Adjustment of RVP must be performed using common blending components from the gasoline stream. At April 1, 1996, the hydrocarbon fraction must also meet specifications for benzene, olefin content, aromatic hydrocarbon content, maximum T90 and maximum T50 found in California Code of Regulations, Title 13, Sections 2262.3, 2262.4, 2262.7, and 2262.8 (T90 and T50), respectively.

<sup>b</sup> RVP range 7.0-9.0 psi for those geographical areas and times indicated for A, A/B, B/A, and B volatility class fuels in Table 1. RVP range 9.0-10.9 psi for those geographical areas and times indicated for B/C, C/B, C/D, and D/C volatility class fuels. RVP range 10.0-13.1 psi for those geographical areas and times indicated for D, D/E, E/D, and E volatility fuels. Geographical areas referenced in this note shall be adjusted to reflect the air basin boundaries set forth in Title 17, California Code of Regulations, Sections 60100 through 60113.

<sup>c</sup> No added lead.

<sup>d</sup> No added phosphorus.



Table 12 California Air Resources Board M100 Fuel Methanol Specification

Specification	Value	Test Method
Methanol	96 vol% (min)	As determined by the distillation range below
Distillation	4.0°C (range)	ASTM D1078-86, at 95% by volume distilled; must include 64.6 + 0.1%
Other alcohols and ethers	2 mass% (max)	ASTM D4815-89
Hydrocarbons, gasoline, or diesel fuel derived	2 mass% (max)	ASTM D4815-89, and then subtract concentration of alcohols, ethers, and water from 100 to obtain percentage hydrocarbons.
Luminosity		Shall produce a luminous flame, which is visible under maximum daylight conditions, throughout the entire burn duration; applicable January 1, 1995
Specific gravity	0.792 + 0.002 at 20°C	ASTM D891-89
Acidity as acetic acid	0.01 mass% (max)	ASTM D1613-86
Total chlorine as chloride	0.0002 mass% (max)	ASTM D2988-86
Lead	2 mg/L (max) <sup>a</sup>	ASTM D3229-88
Phosphorus	0.2 mg/L (max) <sup>b</sup>	ASTM D3231-89
Sulfur	0.002 mass% (max)	ASTM D2622-87
Gum, heptane washed	5 mg/L (max)	ASTM D381-86
Total particulates	5 mg/L (max)	ASTM D2276-89, modified to replace cellulose acetate filter with a 0.8 µm size membrane filter
Water	0.3 mass% (max)	ASTM E203-75
Appearance	Free of turbidity, suspended matter, and sediment	Visually determined at 25°C by Proc. A of ASTM D4176-86
Bitterant	c	
Odorant	d	

a No added lead.

b No added phosphorus.

c The M-100 fuel methanol at ambient conditions must have a distinctive and noxious taste to prevent purposeful or inadvertent human consumption, application January 1, 1995.

d The M-100 fuel methanol upon vaporization at ambient conditions must have a distinctive odor potent enough for its presence to be detected to a concentration in air of no more than 1/5 (one-fifth) of the lower limit of flammability, applicable January 1, 1995.

Table 13 Preferred Property Requirements for Generic and Proprietary Additives

	Emetic	Color	Odor	Denaturant	Corrosion inhibitor	Ignition improver	Lubricant	Detergent
pH Insensitive	←							→
No emissions increase	←							→
Photochemically stable	←							→
Oxidatively stable	←							→
Nontoxic	←							→
Easily detectable		←		→				
No fuel system residue	←							→
No olefin linkage bonds			←	→				
No sulfur or phosphorus	←							→
No ash	←							→
Solubility to -40°F	←							→
Thermally stable	←							→

enable diesel engines to be converted readily to methanol fuel. One such additive, AVOCET, has been successfully used in retrofitted buses in Los Angeles for several years [10, 11, 12].

## 6.7 Methanol Vehicle Exhaust Emissions

As part of the fuel neutral policy being followed by the U.S. administration under the CAAA, all vehicles are, or will be, covered by increasingly stringent exhaust emissions standards irrespective of the fuel being used. It has already been mentioned that the California Clean Vehicle Program sets standards (see Tables 2, 3, and 4) to be attained by increasing percentages of vehicles over the next 20 years. The EPA, on behalf of the federal government, has also issued national standards pertaining to fleet vehicles, with particular emphasis on regulating evaporative emissions in addition to exhaust emissions. Evaporative emissions refer to fuel vapors (hydrocarbons) emitted into the atmosphere as a result of evaporation during fueling or generated as a result of leakage and spillage, or fugitive emissions from the fuel supply lines to the engine or vapor absorption canisters. Fuels that offer low evaporative emissions performance include CNG (because any leak tends to be critical and therefore would be rectified immediately) or any fuel with relatively low vapor pressure at ambient temperature. Engines utilizing such fuels and the vehicles powered by them are identified as inherently low-emissions vehicles (ILEV).

It is fundamental to the establishment of the ILEV concept that a reduction in hydrocarbon emissions results in a corresponding reduction in ambient ozone levels, a view not universally shared. For example, in areas where there is a high concentration of natural hydrocarbons in the atmosphere or where there is a low NO<sub>x</sub>-hydrocarbon ratio, hydrocarbon reductions will have little effect. However, there is sufficiently widespread applicability of beneficial effects arising from lower hydrocarbon emissions, not least when air toxics, such as benzene or 1,2-butadiene, are concerned, that the national ILEV designation is another worthwhile step on the road to clean air.

The impact of ILEV on methanol fuel is dramatic because M85 or any similar fuel methanol formulation is effectively excluded from consideration. The ILEV concept is a carefully constructed transportation control measure designed to encourage the swifter introduction of dedicated vehicles, particularly those fueled by M100 or CNG, provided such vehicles can meet the LEV exhaust emissions standards set by California and the ILEV evaporative emissions standard set by the EPA for the fuel and fuel supply system. The EPA estimates that the ILEV standards offer triple the emissions reductions of a LEV and double those of ULEV [13]. Of course, such estimates beg the question of equivalen-

cy of emissions. For example, is a gram of  $\text{NO}_x$  of equal importance to a gram of, say, carbon monoxide or hydrocarbons?

In practice, exhaust emissions are notoriously difficult to establish for a given engine-vehicle combination because of the number of parameters that can influence significantly both the quantity and the nature of exhaust pollutants. Many of these variables are interactive, and trade-offs between them mean that emissions performance is always a compromise. Nevertheless, the CARB LEV standards can be readily met by dedicated methanol engines, both M85 and M100 fueled. The vapor pressure of M85, on the other hand, leads to problems with the evaporative emissions criteria. Figure 7 illustrates the vapor pressure of methanol containing varying quantities of gasoline, showing clearly the penalty each fuel suffers by virtue of its incompatibility with the other.

## 6.8 Future Methanol Engines and Vehicles

The twin forces driving the move toward alternative fuels energy security and air quality are mutually supporting in the sense that EPA's CAA is air quality neutral whereas CAAA is fuel neutral. Legislation is therefore encouraging the cleanest, most economical alternative transportation fuel capable of being supplied nationally from domestic sources. However, a fuel is only "clean" in the context of its use to power an engine, so it is the distribution-fuel-engine system that must be assessed. In California, there is set out a clear progression to the cleaner system already discussed (Tables 2 and 3). Methanol fuel-vehicle systems must be developed to meet not only the needs of California, but also the national standards promulgated by the EPA. Currently an evolution of methanol-fueled

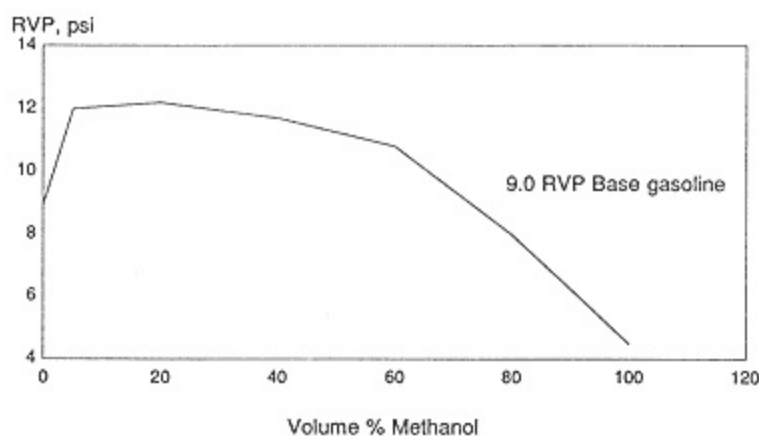


Figure 7  
Reid vapor pressure of methanol/gasoline mixtures.

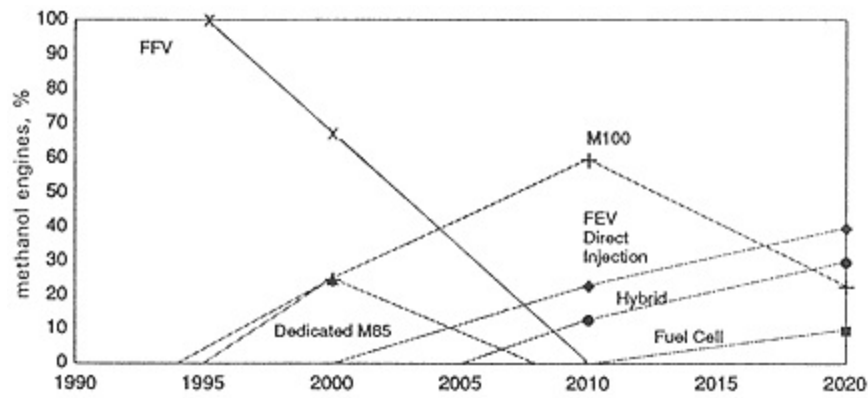


Figure 8  
Evolution of methanol engine technology.

engines to meet clean air requirements is beginning to unfold. Any view of the future of a particular technology, especially one so quickly moving as clean-air vehicles, is fraught with more than the usual uncertainty. However, Figure 8 shows a reasonably defensible outlook that envisions a transition from gasoline to dedicated by hybrid to fuel cell methanol vehicles over the next 25 years. Central to future methanol vehicles is the concept of an engine family dedicated to M100 operation and fully utilizing all the features methanol can offer as a clean and efficient [14] fuel. Such an engine has been developed by FEV under a project initiated by the EPA [15]. It involves a direct-injected high-compression engine configured to minimize emissions and maximize fuel economy. Figure 9 gives some data on this engine and its performance parameters. Of

Emissions in grams per brake horsepower hour

	NMOG	CO	NOx	Aldehydes	Particulates
LEV	0.075	3.4	0.2	0.015	0.08
ULEV	0.040	1.7	0.2	0.008	0.04
FEV DI	0.100	0.1	0.16	0.002	0.03

Fuel Economy (miles per gallon diesel fuel equivalent):  
 38.3 Federal Test  
 57.5 Highway Fuel Economy Test

Note: This engine started at 30°C, and is expected easily to reach ULEV standards with further development.

Figure 9  
Emissions and performance of the FEV direct-injected methanol engine.

particular interest is the idea of utilizing this type of engine to power a hybrid vehicle. This concept embodies the best features of batteries and methanol by running a methanol-fueled FEV engine continuously at a constant load optimized for lowest emissions and directing the power either to drive the vehicle or to charge a battery, whichever is demanded. Peak power is obtained by taking energy from both the battery and the engine. In this way, a small engine with its lower (and optimized) emissions can yield emissions results close to ZEV, without suffering the disadvantages of a large engine (higher emissions and intermittent operation) or a large bank of batteries (cost and limited life at high power).

## 6.9

### Methanol in Heavy-Duty Engines

Methanol is an efficient high-octane fuel for gasoline engines, which means that it possesses poor compression ignition characteristics in diesel engines. In other words, the ability of methanol to suppress ignition translates into a low cetane number in diesel engines, in which the ability to ignite fuel readily at temperature produced by air compression in the cylinder is critical.

Consequently, the task faced by diesel engineers in designing a diesel cycle engine fueled by methanol is considerably more difficult than the equivalent for a spark-ignited engine. Various approaches to achieve facile ignition of methanol under diesel conditions have been tried, including electrical ignition by spark plug or glow plug; ignition-improving additives, such as AVOCET; very high compression ratios ( $>22:1$ ); dehydrating some methanol to dimethyl ether before injection; and pilot ignition with diesel fuel. All these approaches work, but successful engines have used one or more combinations of the first three.

Most progress has been made in the heavy-duty transit bus engine market, dominated in the United States by the Detroit Diesel Corporation. This market segment was explicitly chosen by the EPA to pioneer alternatively fueled diesel engines because buses operate in the midst of people and so give rise to a disproportionate number of complaints regarding smoke emissions and odor. They are also relatively easy to regulate since they are centrally fueled, funded in part by public funds, and operate within a well-defined and limited geographical area.

By 1993, the Detroit Diesel Corporation (DDC) had taken a commanding lead in heavy-duty methanol engine development, with over 400 buses in revenue service within North America, powered by a methanol version of the well-proven 6V92 engine [16]. This engine uses a 23:1 compression ratio, requires glow plugs for starting up, and was the first heavy-duty engine to be certified for transit bus use by both the EPA and CARB (Tables 14 and 15). At the same time, the

Table 14 EPA Standards for Heavy-Duty Diesel Engines (Including Buses) and DDC 6V92-Certified Emissions Data

	Emissions (g per brake hp-h) EPA transient test procedure				
	Hydrocarbons	NOx	CO	Particulates	Aldehydes
EPA 1991	1.3	5.0	15.5	0.25	Not regulated
EPA Urban Bus 1993	1.3	5.0	15.5	0.10	Not regulated
EPA 1994	1.3	5.0	15.5	0.10	Not regulated
EPA Urban Bus 1994	1.3	5.0	15.5	0.05a	Not regulated
EPA 1998	1.3	4.0	15.5	0.11	Not regulated
EPA Urban Bus 1998	1.3	4.0	15.5	0.05a	Not regulated
DDC Certification (1992) with M100 Fuel	0.1	1.7	2.1	0.03	0.10

a EPA can set at 0.07.

capacity of ignition improvers to allow methanol to ignite compressively opened up the option of converting existing buses to run on methanol. This technology has been brought to fruition in Los Angeles by the former Rapid Transit District (now part of the Metropolitan Transit Authority), where 12 such retrofitted buses have been running successfully for several years in revenue service in South Central Los Angeles.

Additional heavy-duty engines under development include the Navistar 466 DT and DDC 471 and 8V92, and market penetration is beginning to open up

Table 15 CARB Urban Bus Standards for DDC 6V92TA-Certified Emissions Data

	Emissions (g per brake hp-h)				
	Hydrocarbons	NOx	CO	Particulates	Aldehydes
M100	0.1	1.7	2.1	0.03	0.07
M85	0.2	4.1	1.6	0.03	0.08
M99 + 1% AVOCETa	0.2	4.0	0.6	0.04	0.18
1994 CARB Urban Bus Standards	1.3	5.0	15.5	0.07	0.10
1996 CARB Urban Bus Standards	1.3	4.0	15.5	0.05	0.10

a Results achieved without optimization.

other segments, including stationary generators, school buses, paratransit vehicles, and other medium- to heavy-duty applications. Outside the United States, Volvo, Saab-Scania, and Daimler-Benz have been particularly active in developing heavy-duty methanol engines, without as yet widespread commercialization taking place.

## 6.10

### Outlook for Fuel Methanol

The future of alternative fuels in the United States, and the role of methanol in that future, is difficult to predict with any certainty. There is no question that alternative fuels will capture a fraction of the total U.S. transportation fuel market; the uncertainty revolves around how large the portion will become and over what time period.

The major imponderables determining the extent of use and rate of penetration of alternative fuels are as follows:

- Future price of crude oil

- Congressional determination to tackle energy security

- Administrative willingness to apply the CAAA

Beyond the general question of alternative fuels usage, the probability that methanol in particular will achieve a significant proportion of alternative fuel growth as a transportation fuel must be assessed. That the merits of methanol make it the only alternative fuel suitable for widespread distribution (see Table 16) does not guarantee it a significant role in transport. This is simply because conventional fuels in the form of reformulated gasoline (RFG) or "clean diesel," together with advances in engine technology, such as close-coupled preheated catalysts for cars and advanced electronic controls for diesels, make it likely that gasoline and diesel will continue to be major fuels. Indeed, it could be argued that the main role of alternative fuels has been to galvanize the transportation industry into developing cleaner fuels and technology. Without the stimulus (i.e., threat) posed by methanol, it is certain that neither RFG nor clean diesel would have made an appearance on the fuels scene.

A further major factor holding back the expansion of methanol is competitive pressure from CNG. There are those who claim that the deployment of massive, and frequently rate-based, resources by natural gas utilities does not in fact detract from the rate of growth of methanol because each fuel has its own market niches in which it is paramount, and in any case, the potential market demand is so large that there is more than enough room for both. Such claims are illusory: they ignore the fact that there are limited commitment, resources, and financing available to federal, state, and municipal governments to facilitate the



Table 16 Merits and Disadvantages of Fuel Methanol

Methanol is the only alternative fuel offering all these attributes:

- Capable of meeting lowest PM and NOx requirements
- Liquid at room temperature
- Available from domestic sources for all U.S. needs
- Accessible via conventional infrastructure
- Supplied by open market competition
- Supported by proven engine technologies
- Ultimately fully cost competitive as demand increases
- Comparatively risk free

Currently methanol suffers from the following disadvantages:

- Potential formaldehyde emissions
- Higher cost per Btu
- Toxic to humans
- Low flame luminosity
- Vapor-phase explosivity
- Cold start difficult (M100)
- Lower energy density (versus gasoline)

advancement of fuels. If those finite resources are committed to CNG because of the disproportionately large influence and funds that the natural gas industry can bring to bear, then there is no residual enthusiasm or revenue left for the relatively tiny and underrepresented methanol industry (it should be borne in mind that the natural gas industry is three orders of magnitude larger than the methanol industry). Similar reasoning applies to the engine manufacturers: limited engineering and development efforts are overwhelmed by funds made available for CNG engine development by the gas industry. The distortion, which this heavy bias brings to even-handed development of alternative fuels based upon their true merits, is probably the most serious and underappreciated handicap currently prejudicing the future of fuel methanol.

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## 7

## Agriculture and Methanol

Arthur M. Nonomura

Arizona State University, Tempe, Arizona

Andrew A. Benson

Scripps Institution of Oceanography, La Jolla, California

Deepak Nair

Methanex Inc., Houston, Texas

## 7.1

## Introduction

Modern agriculture is intensive and integrates financial, social, and mechanical as well as scientific biological aspects. Crop productivity has attained optimization by effectively integrating biochemistry, applied engineering, crop physiology, tillage, fuel energy, genetic, and educational considerations. Handling bulk quantities of pure chemicals on farms is generally well-understood; however, the same degree of familiarity is not shared by the methanol industry with agriculture. Important resources in the overall picture of improving crops in modern agriculture include such elements as regulatory agencies, land, water, electricity, fuel, machinery, transportation, marketing, and agricultural chemicals, but the methanol industry has previously only participated indirectly in the use of methanol as a chemical intermediate or feedstock for the synthesis of agrichemicals: methanol is utilized in some agrichemicals as a carrier.

Agricultural resources are limited and the burgeoning pressures of massive increases in the population of the world drive competition for them by urban and rural sites. Thus, as the stewards of the land are giving way to the encroachment of territory by urban requirements, agriculture is met with the challenge of increasing the efficiency of production with fewer raw materials. Technologies to improve the efficiency of photosynthetic production that have been in-

roduced within the past two decades include the provision of aqueducts to irrigate farmland with high insolation, intensive planting designs, and, to a lesser degree, adjustments of anatomy to reduce self-shading and increase light interception. Efforts to breed plants with improved photosynthetic efficiency have not been successful. Improvement in crop efficiency is at a state of high demand, but the potential for development from classic resources has been all but exhausted.

Terrestrial crops are inefficient light energy-gathering systems in which 13% or less of the sun's energy that is intercepted by green plants is transformed into biomass. Dry land crops grown under nearly optimal conditions with irrigation and complete major nutrient and micronutrients availability generally show an upper limit of 1% net solar energy conversion to harvested total biomass. In part, this low efficiency of solar conversion by plants is explainable by such physical considerations as photosynthetically active radiation, which constitutes 43% of the total incident solar radiation energy, but other factors, such as arrangement of leaves and adaptive anatomy, are involved. It is possible, for instance, to calculate energy conversions as high as 3% for plants with Kranz anatomy, C<sub>4</sub> metabolism, and low rates of photorespiration. These photosynthetically efficient plants, generally referred to as C<sub>4</sub> plants (plants for which the first product of photosynthesis is a four-carbon sugar), are generally tropical weeds and comprise a few of our major food crops, that is, corn, sugarcane, sorghum, and amaranth. C<sub>4</sub> plants generally have higher light intensity, drought stress, and heat tolerances than C<sub>3</sub> plants (plants for which the first product of photosynthesis is a three-carbon sugar). With rare exceptions, all other major food crops are C<sub>3</sub> plants in which photorespiration can occur at sufficiently high rates to stop growth for several hours per day. Sunflower is one of the rare C<sub>3</sub> plants that is adapted to very high light intensities and other conditions that would otherwise cause high rates of photorespiration under clear afternoon skies.

In the sun belt under the midday sun, light energy may often be dissipated by heat, a complete waste, contributing greatly to the inefficiency of the lightgathering system of green plants. Considering an evolutionary perspective, this low efficiency with light is attributable to an atmospheric carbon dioxide deficiency in plants within the C<sub>3</sub> category. Air contains only about 0.033% carbon dioxide, but 20% oxygen. Oxygen competes for the same binding sites as carbon dioxide, that is, for the enzyme ribulose biphosphate carboxylase. When oxygen uptake outcompetes carbon dioxide uptake by plants in light, the plant is photorespiratory. Net carbon dioxide uptake decreases with greater rates of photorespiration and reverses the overall reaction of photosynthesis as sugar is converted back to carbon dioxide and water. At high light intensities characteristic of direct midday sunlit fields with clear skies, the top leaves of a C<sub>3</sub> plant,

which are photorespiratory, show reduced net photosynthesis. Lower leaves in the canopy, which are shaded, may not show photorespiratory stress attributable to very high light intensities because they are shaded. In the field at sea level, the very high light intensities at noon are often associated with high temperatures and water stress, which make the stomata close. When the stomata close, the entry of carbon dioxide into the leaves is reduced, which can result in more photorespiration. Theoretically, the control of photorespiration across the food crops of the world could as much as double yields, but previous attempts at such control were not feasible utilizing conventional technologies. For example, increasing the concentration of carbon dioxide in the atmosphere surrounding plants increases vegetative yield, but the daily cost of the extra carbon dioxide (e.g., \$5000 per acre) far exceeds the returns. Alternatively, culture of crops by frequent irrigation to relieve photorespiratory stress has been recommended, but the direct cost of water is high in most areas. Add to this the indirect costs attributable to high levels of irrigation, including weed control, erosion, more labor, added cultivation and land-leveling requirements, water table depletion, correction of pollution, and lack of field entry, and the cost of increased water demands becomes prohibitive. For responsive crops that are inexpensive commodities, technologies that decrease irrigation requirements without stress by inhibiting photorespiration may be of benefit to the grower. An economical means of inhibition of photorespiration has been sought for decades, and methanol may well provide the solution.

Plants have a limited capability for absorption of aqueous nutrients through foliage, but with the addition of methanol, penetration is enhanced. Rapid uptake of methanol by plant tissues has been known for decades, and more recently, the metabolism of methanol in minutes by passage through tetrahydrofolate to serine and subsequent sugars has also been understood for years. As was recently determined by the Agricultural Laboratory of the Arizona Department of Agriculture (R. A. Sinnott, 1993), the uptake of methanol by plants in light leaves no significant residual methanol above baseline as detectable by as chromatography within 1530 min of penetration. Treatment of plants with methanol is therefore an inexpensive, safe, and effective means of providing plants with a source of fixed carbon and carbon dioxide. The metabolism of methanol is a natural consequence of the degradation of cell wall materials, particularly pectin, in plants: hence the early nomenclature, wood alcohol.

Methanol is a concentrated liquid source of carbon for plants, but only very low concentrations (usually less than 1% methanol) were previously utilized in laboratory studies, higher concentrations generally having been found to be toxic to plant tissues. As a carbon nutrient source for plants, application of 1% methanol to crops is not economically feasible, but if a method existed by which the

input of much higher concentrations of methanol could be achieved, the carbon input would be that much more significant. Nonomura and Benson [1] recently established that the application of concentrations of 10-100% methanol to some crops increased photosynthetic productivity. Plant metabolism of concentrations of methanol that were previously considered toxic was achieved by application with high-intensity sunlight. Laboratory investigations [26] and field observations support indications that methanol inhibits photorespiration. Benson and colleagues [4,5] concluded that safe treatment of plants with methanol was most effective when applied under conditions consistent with lengthy periods of photorespiration.

"Photorespiration" is a biochemical term describing plant uptake of oxygen in light outcompeting carbon dioxide uptake in light. Oxygen uptake is catabolic and results in the breakdown of sugars that were made previously during photosynthesis. Photorespiration is greatest under conditions of high light intensity, high temperatures, and wind and water stress. Lengthy periods of high rates of photorespiration are often physically manifested by midday wilt. An economically feasible means of inhibiting photorespiration was not achieved until the discovery by Nonomura and Benson that foliar treatments with relatively high concentrations of methanol increased plant growth in a manner consistent with the reduction of photorespiration.

## 7.2 Mechanism

The methanol molecule is smaller than carbon dioxide and penetrates most plant tissues quickly for rapid metabolism. As a plant source of carbon, methanol is a liquid concentrate: 1 cc methanol provides the equivalent fixed-carbon substrate of over 2,000,000 cc of ambient air. Methanol absorbed by foliage is metabolized to carbon dioxide, amino acids, sugars, and other structural components. Two major paths of methanol metabolism are the internal production of carbon dioxide that is then utilized in photosynthesis and the incorporation of methanol as a fixed source of carbon. Briefly stated in field terms, methanol treatments are a means of placing carbon directly into the foliage. High light intensity is necessary to drive photosynthesis at the rates necessary to process the high internal levels of carbon dioxide presented by methanol. Serine formation and carbon dioxide fixation by photosynthesis may lead to the production of sugar. Increases of sugar concentration in the presence of moisture lead to increased turgidity.

Methanol treatments of C<sub>3</sub> plants have been found to result in growth improvements, but methanol on C<sub>4</sub> plants does not enhance growth. This observation is consistent with the inhibition of photorespiration by methanol since C<sub>4</sub> plants have very low rates of photorespiration under high light intensities.

## 7.3

### Field Observations

Several crops that are particularly responsive to treatment with methanol in Arizona desert regions include watermelon, tomato, strawberry, eggplant, chili, and lettuce. These plants have C3 metabolism in common, but they are also misplaced plants in the desert. Optimal culture of these plants was developed for the temperate zone. Under summer conditions of the desert, these plants become highly photorespiratory. When methanol is utilized to inhibit photorespiration in these plants, increased photosynthetic productivity results. In other words, with methanol treatments, the high-intensity sunlight energy input that is characteristic of the desert is no longer dissipated as heat by crops, but is instead put to use to make sugars and other plant structural components. Light energy is utilized with greater efficiency than normal when methanol is applied to plants in a timely manner. The increase in photosynthetic productivity in the plant is therefore directly related to the subsidence of midday wilt attributable to methanol applications to crops in the desert. Environments, such as northern latitudes, in which optimal growth of plants is achieved normally will not benefit from methanol treatments, but if crops in the northern latitudes show lengthy periods of high rates of photorespiration, for example, during hot periods, with water stress far exceeding the historical norms, then a significant potential for growth improvement exists. Under stressless conditions, plants do not exceed optimal growth potentials by the addition of methanol. In the desert environment of the Valley of the Sun in Arizona, most crop plants are misplaced: that is, optimal growth is rarely achieved because the majority of the summer and autumn seasons are given to clear skies, with very high light intensity, daily high temperatures exceeding 40°C, and low humidity with high winds contributing to severe water stress. Under such arid environments, high rates of photorespiration, which slow growth substantially, are likely to be observed in C3 plants. Appropriate treatment of plants with methanol in the desert environment is therefore likely to enhance growth to fulfill optimal potential. For example, lettuce was treated with diluted methanol several times in a trial undertaken by Professor William Molin at the University of Arizona during the summer. In these tests, lasting 5 weeks, small lettuce plants treated with methanol in the greenhouse showed significantly higher vegetative shoot yields than controls that were treated with water and surfactant (see Figure 1). The populations compared were small, as indicated by the low values given for degrees of freedom, but the probability of sameness between test and control populations indicates a significant improvement in growth when plants were treated with methanol.

Similar results have been observed consistently in the desert agriculture of other food crops with C3 metabolism [7], but improved photosynthetic productivity was not observed in C4 crops, such as corn.



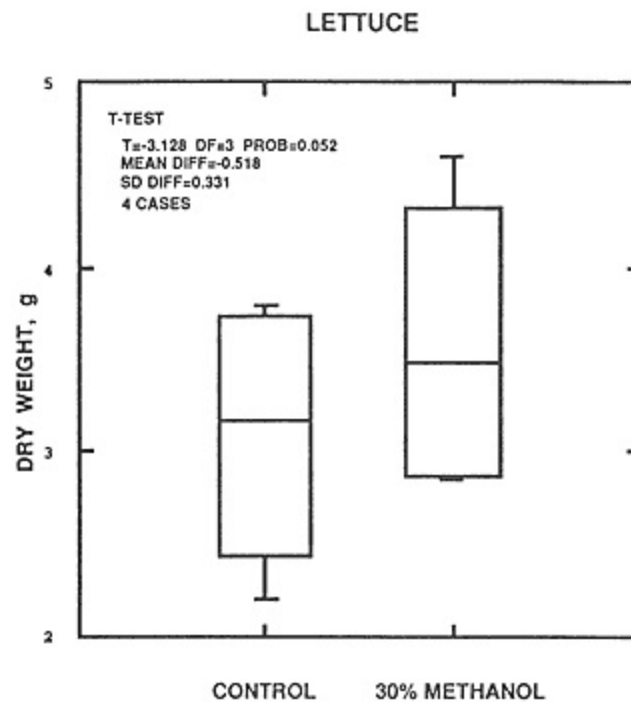


Figure 1

Effect of methanol treatment on the growth of lettuce.

The spring and summer of 1993 were dedicated to systematizing the necessary protocols for methanol application to crops, a large number of field tests being conducted around the world. It is clear that growers and scientists who have followed protocols specifically designed toward nutrient amendment and the exploitation of the photorespiratory pathways have succeeded in improving the growth of plants with methanol (e.g., Ref. 8). Compromising protocols or disregarding the environmental factors prerequisite to methanol utilization on crops may not show such clear benefits.

## 7.4

### Conclusion

When applied to C<sub>3</sub> crop plants under conditions consistent with lengthy periods of high rates of photorespiration, methanol contributes to the nutrification of foliage and is likely to improve photosynthetic productivity substantially. Photorespiratory stress can be induced artificially by controlling environmental



factors or introduction of photorespiratory metabolites and provides a means of safe and effective treatment with methanol.

Photosynthesis and photorespiration are of the highest orders of scientific complexity and the application of methanol to crops poses certain need for mechanistic studies as well as continual practical consideration and reduction of safety and handling risks. Therefore, it should be cautioned that end users should not rush out to spray methanol. It is hoped that a defined formulation and protocol will be ready for the grower after all data have been carefully digested. Then, and only then, with custom-designed distribution of methanol products for crops, can humanity begin to gain maximum benefit and enjoyment from this discovery.

We conclude that treatment of crops with methanol has the potential to improve photosynthetic productivity under a variety of conditions, but it is economically favored under the very high light intensities typical of agricultural crops in the sun belt particularly for alternative crops. Methanol is the least expensive of industrially manufactured fixed-carbon nutrient sources for plants. As the mechanism of action of methanol on photosynthesis is elucidated, it is quite likely that other plant treatments will be designed for ever greater efficiencies of light energy capture. Factoring in the low commodity cost of methanol, however, ensures its utilization in agriculture over a very long future.

### Recommended Sources for More Information

Estrella Mountain Community College Center, 3000 North Dysart Road, Litchfield Park, AZ 85340-4937; FAX (602)935-8060.

Arizona Department of Agriculture, 1688 West Adams, Phoenix, AZ; FAX (602)542-5420; regulatory and safety inquiries.

State Fire Marshall, 1540 West Van Buren, Phoenix, AZ 85007; (602)255-4964; permits for handling more than 10 gal methanol are obtained here.

Estrella Rotary Rose Company, P.O. Box 236, Litchfield Park, AZ 85340; the most sensitive bioassay plant is the Paul Harris Rose.

Industrial Commission of Arizona, Division of Occupational Safety and Health, 800 West Washington Street, Phoenix, AZ 85007-2922.

Arizona Department of Transportation, Transportation Safety Office, 531M, P.O. Box 2100, Phoenix, AZ 85001-2100.

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## 8 Other Applications

Chauchyun Chang  
Union Chemical Laboratories/Industrial Technology Research Institute, Hsinchu, Taiwan,  
Republic of China

Wu-Hsun Cheng  
Chang Gung College of Medicine and Technology, Kweishan, Taoyuan, Taiwan, Republic  
of China

### 8.1 Introduction

Methanol applications can be divided into three major end-user categories: chemical feedstock, fuel and fuel additives, and miscellaneous applications. The first two users cover more than 95% of methanol consumption and are discussed in the previous chapters of this book [1, 2]. This chapter focuses on various methanol applications that are not covered in previous discussions. Most of these applications utilize the physical properties of methanol, except for the production of single-cell protein and sewage treatment, which use methanol as a substrate to supply the energy needed in the growth of microorganisms. A brief discussion of each of these applications of methanol is given.

### 8.2 Single-Cell Protein

#### 8.2.1 Historical Development

Single-cell protein (SCP) is the term that refers to protein in a variety of microbial cells, which are produced by fermentation using hydrocarbon substrates. The typical protein content of these microorganisms is 6070% in bacteria, 4565% in yeasts, and 3540% in mold after separation and drying [3]. When

properly produced, these protein concentrates can be used as an animal feed substitute or a nutritional source for human food [39].

The use of microorganisms in human food has been practiced since ancient times. Yeast has been used in baking and brewing for thousands of years. Cultured dairy products, such as yogurt, cheese, sour cream, and buttermilk, contain millions of cells of lactic acid bacteria and are another example of the microorganism application in human food. However, the first modern effort to produce microbial cells for human food or animal feed emerged in Germany during World War I, when Baker's yeast, *Saccharomyces cerevisiae*, was produced [4]. In the period between World War I and World War II, several processes were developed in Germany and Finland to produce fats and fodder yeasts from sulfite-containing wastewater. During World War II, extensive research was undertaken in Germany to produce food by torula yeast, *Candida utilis*, from sulfite-containing wastewater [4, 5].

However, the modern history of SCP stemmed from research work by the petroleum industry in the late 1950s on the removal of wax and sulfur fractions from crude oil using microorganisms. It was found that certain microorganisms can assimilate only the paraffinic hydrocarbons, and these microorganisms in the effluent of the dewax process contain over 50% of high-quality cell protein, rich in amino acids [5]. This observation resulted in one of the most attractive research projects to produce materials suitable for animal feed substitute or a nutritional source for human food during the 1960s to 1980s.

N-paraffins and gas oil (contains 1020% linear paraffins) were the original substrates chosen for SCP production. The trace of n-paraffins left in the SCP using n-paraffins or gas oil substrate has suspected carcinogenicity, however, and may build up in the tissue of animals fed by these SCP. This problem caused resistance of customers to buy animals fed with the SCP. Under this circumstance, methanol was chosen as a substitute because [10] (1) it has high solubility in water; (2) it possesses low explosion hazard; (3) it is readily available with high purity; (4) it needs less oxygen for metabolism than n-paraffins; and (5) it has a lower cooling load than n-paraffins.

Although methanol can be used as a substrate to produce SCP from bacteria, yeasts, and molds, most of the research on methanol SCP was focused on the production of bacteria [1022]. The major advantages of bacteria over yeasts can be summarized as follows [4, 5, 10]: (1) bacteria have a high protein content, with the dry cell containing up to 80% crude protein; (2) they have a high doubling rate; and (3) they do not possess toxicity or pathogenicity. Bacteria are much smaller than yeasts, however, which makes them more difficult to separate and break. This difficulty results in a high production cost, a problem that must be solved to develop an economical commercial production process.

## 8.2.2

### Commercial Production Technology

During the 1960s to 1980s, many companies spent a considerable amount of money on research and development in an attempt to develop commercial processes for the production of bacteria from hydrocarbon substrates [5, 8, 1322]. Most of these companies are chemical and petrochemical companies that have very little direct interest in the animal feed or human food business.

ICI [2226], Phillips Petroleum [19, 21], and Hoechst [15] are some of a few companies that have worked on commercial process development for bacteria production using methanol substrate. However, only ICI has built a 60,000 ton per year plant at Billingham, England. It produces SCP for animal feeds with the brand name Pruteen [4]. The bacterium chosen for the ICI process is *Methylophilus methylotrophus*, which utilizes methanol as a source of carbon and energy and ammonia as a source of nitrogen [3, 5, 10]. Figure 1 [4, 5, 10, 2326] shows a schematic flowsheet for the production of SCP using a methanol substrate.

Bacterium seeds, water, and methanol are fed into an inoculation tank. Sterilized air and nutrients are then injected into the fermenter along with an inoculum of cultivated bacteria. Ammonia is added as a nitrogen source and for pH control. Continuous fermentation produces a steady stream of bacteria, which are sent into a flocculation tank after filtration and centrifugal separation. The concentrated effluent from the flocculation tank is further dewatered by a series of decanter centrifuges. SCP destined for human consumption must undergo an additional step to remove the nucleic acids contained in the cells by one of the following techniques [4]: (1) acid hydrolysis, (2) cell disruption, (3) chemical extraction, (4) alkaline hydrolysis, or (5) enzymatic treatment. Finally, the concentrated product stream is dried and processed into granules, pellets, or powder and then packed for sale. The overall yield is 1 ton protein for every 1.8 ton methanol consumed in the process.

The development of the commercial process encountered two major engineering problems [10, 2426] that had to be solved to reduce the production cost to an economical level. The first problem was the design of a new type of fermenter, which is the heart of the entire process. The conventional, mechanically stirred fermenter has the following drawbacks [10]: (1) it cannot be extrapolated to large (over 1000 m<sup>3</sup>) unit size without loss of efficiency; (2) it can cause severe economic penalties for the single-stream concept adopted in SCP production; (3) it has high energy demands associated with cooling, aeration, and agitation; and (4) it has a low process air utilization efficiency because of the need to maintain a high driving force for oxygen transfer. To overcome these drawbacks ICI developed a "pressure cycle fermenter" [10, 2328]. This type of fermenter, as shown in Figure 2, consists of vertical columns connected at

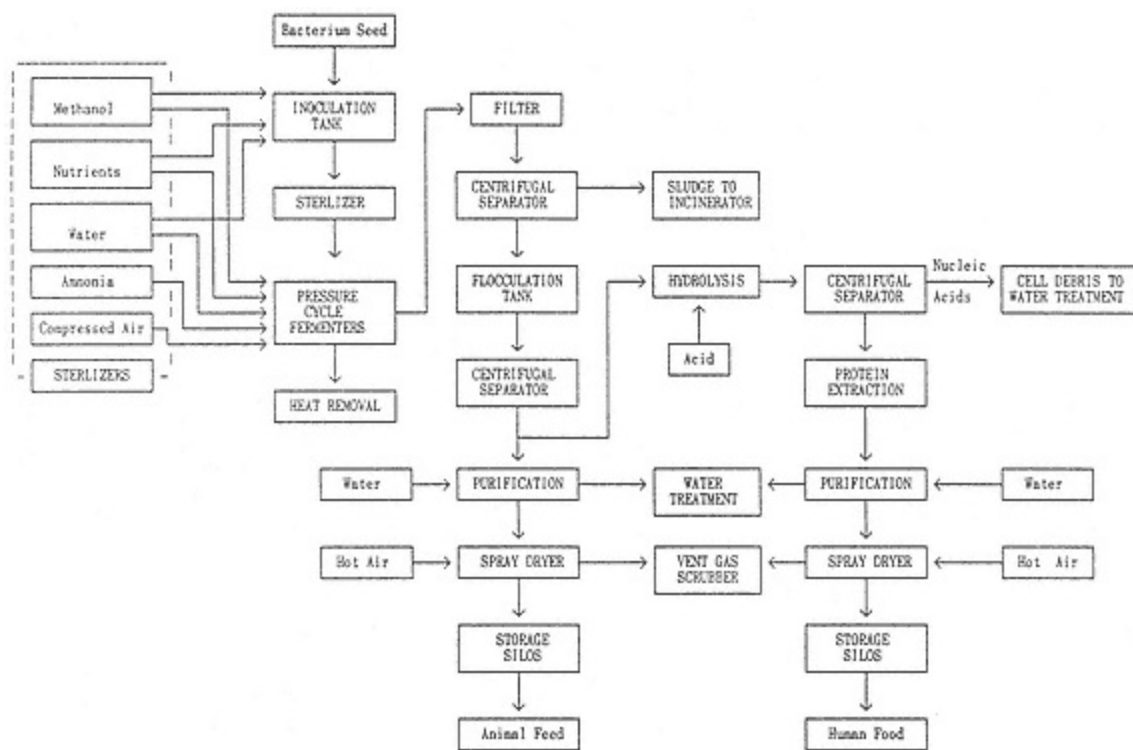


Figure 1  
Methanol SCP production process.  
(From Refs. 4, 5, 10, and 2326.)

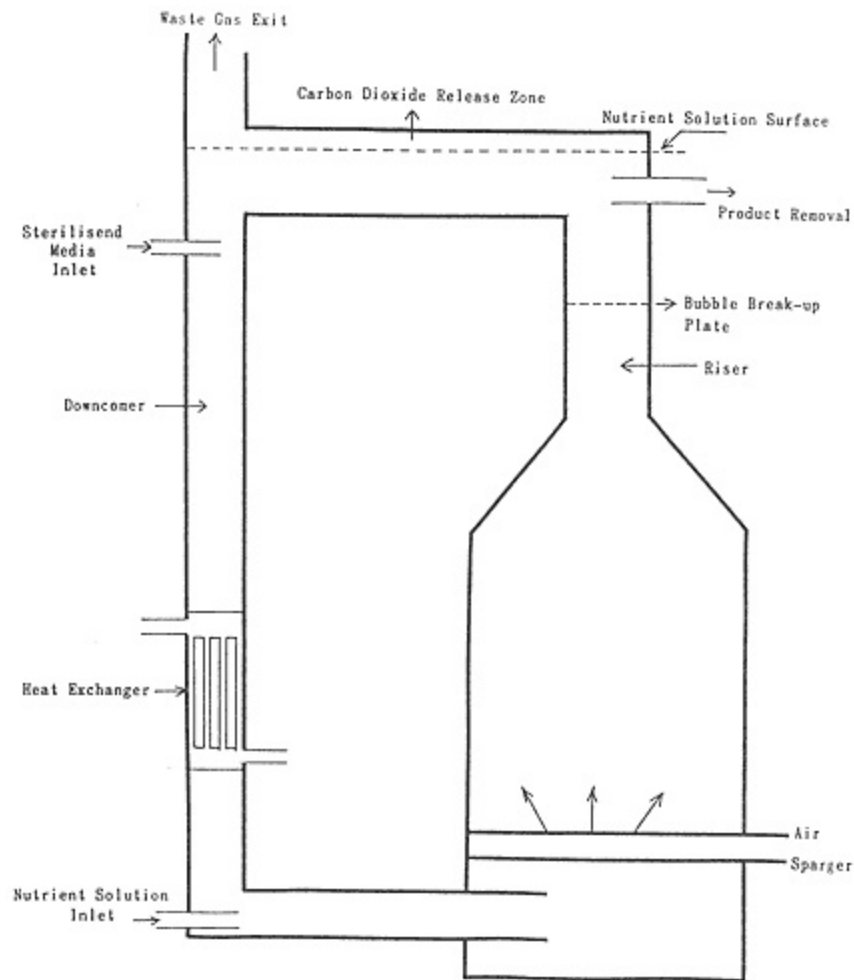


Figure 2  
ICI pressure cycle fermenter.  
(From Refs. 10 and 2328.)

the top and bottom by horizontal sections. The lower horizontal section and the vertical columns are full of fermentation culture, and air is injected into the base of one of the vertical columns to form bubbles. The bulk density of the column contents is reduced in comparison with that in the other column, and the liquid is thus caused to circulate around the system by an airlift effect. This vertical column contains a two-phase mixture of air and culture with a porosity of up

to 50%. Most of the oxygen transfer takes place in this section. The transfer rate decreases as the culture flows to the upper horizontal section of the fermenter when the air becomes exhausted, and the hydrostatic pressure decreases. Carbon dioxide desorption increases toward the top of the fermenter. The spent air is disengaged from the culture, which flows into the downcomer section and is then directed into the vertical column, picking up fresh air and completing the pressure cycle.

The second engineering problem was the separation of bacteria from the supernatant fluid [10, 2328], because the bacteria used are about 1  $\mu\text{m}$  in size and have a density close to that of water. Consequently, recovery by conventional centrifugal separation would require a very large installation that would be extremely expensive. Therefore, the development of a viable SCP process would be prevented without an economical recovery system. The ICI process includes stages of agglomeration and preseparation techniques to tackle this problem. The resulting wastewater and residual substrates are purified and recycled. The agglomerated bacteria cell concentrate can then be further dewatered by conventional centrifugal separation. Of the ingoing solids 99% are recovered as a cell cream comprised of 25% solids. A high concentrate of the centrifuge cream product is required since the final drying is, by an order of magnitude, the most expensive dewatering step.

### 8.2.3

#### Nutritional Value

The structures of bacteria are extremely complex. Nitrogen in particular is distributed in many types of chemical structures, including proteins (amino acids), peptides, nucleic acids, and amino sugars [3, 4]. The amino acid content of bacteria is the best indicator of the overall nutritional utility to animals and humans. Component analyses and the amino acid content of methanol SCP, fish meal, soybean meal, and nonfat dried milk (NFDM) are listed in Tables 1 and 2, respectively [4, 10]. The protein content of methanol SCP is about 80%, which is much higher than that of the other types of food meals. Furthermore, the overall quality of methanol SCP is very good. As a result, it has often been sold at a premium over alternative protein sources.

### 8.3

#### Sewage Treatment

Methanol is used in the point source tertiary sewage treatment facility as an oxidizable organic substrate to provide energy to the bacteria used in the biological nitrification-denitrification process. This process is often the best process available for the removal of nitrogen for the following reasons: (1) high potential removal efficiency, (2) high process stability and reliability, (3) relatively



Table 1 Component Analysis of Methanol SCP and Food Meal (% of Total)

Component	Methanol SCP	Fish meal	Soybean meal	NFDM
Moisture	5.0	10.4	13.0	3.2
Crude protein	79.8	62.3	45.7	36.2
Ash	8.2	16.3	3.6	7.9
Crude fiber		0.5	5.9	
Fat	7.0	4.5	1.3	0.8
Carbohydrates		6.0	31.4	52.0
Total	100.0	100.0	100.0	100.0

Source: From References 4 and 10.

Table 2 Amino Acid Content of Methanol SCP and Food Meals (g Amino Acid per 100 g Dry Material)

	Methanol SCP	Fish meal	Soybean meal	NFDM
Alanine	5.7			1.2
Arginine	3.7	3.9	4.7	1.3
Aspartic acid	7.1			2.7
Cystine	0.5	0.5	0.8	0.3
Glutamic acid	8.0			7.6
Glycine	4.2	3.2	1.6	0.8
Histidine	1.5	1.5	1.2	1.0
Isoleucine	3.6	2.4	2.1	2.2
Leucine	5.6	3.0	3.3	3.5
Lysine	4.9	4.3	2.8	2.9
Methionine	2.0	1.2	0.5	0.9
Phenylalanine	2.9	2.1	1.9	1.7
Proline	2.5			3.5
Serine	2.8			2.0
Threonine	3.8	2.4	1.6	1.6
Tryptophan	0.7	1.3	0.5	0.5
Tyrosine	2.6	1.8	1.5	1.7
Valine	4.3	2.8	2.3	2.4
Total	66.4	30.4	24.8	37.8

Source: From References 4 and 10.

easy process control, (4) low land area requirement, and (5) moderate cost [29]. The process is used to reduce excess nitrogen compounds in two steps with the help of different microorganisms. The excess nitrogen compounds have contributed to the eutrophication of water. In the first step, ammonia is converted aerobically to nitrate ( $\text{NO}_3^-$ ; nitrification). In the second step, nitrate is converted to nitrogen gas in the absence of oxygen (denitrification). Methanol is chosen as the energy source for the microorganisms used in the denitrification process because [30] (1) it gives the highest denitrification rate; (2) it is readily available and its price is relatively cheap; and (3) residual methanol can be removed from the treated effluent by aeration.

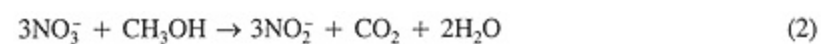
Most of the microorganisms used for denitrification are heterotrophic microorganisms that oxidize organic compounds, but certain autotrophic bacteria using inorganic energy sources are also effective for denitrification. A wide variety of facultative microorganisms are used for denitrification, including *Alcaligenes*, *Bacillus*, *Pseudomonas*, and *Micrococcus*. They are readily available in sewage [31, 32]. These microorganisms have different performance characteristics: some can reduce nitrate to nitrite only, some nitrite to nitrogen only, and some both nitrate and nitrite to nitrogen.

The reaction of nitrogen compounds in the denitrification process proceeds as follows [29, 33]

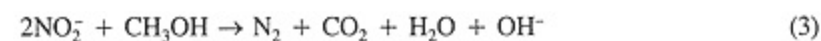
Remove dissolved oxygen in the effluent:



Reduce nitrate ion to nitrite ion:



Convert nitrite ion to nitrogen gas and remove it from the effluent:



Methanol is also used as an energy source for bacterial growth, which requires about 30% of the stoichiometric amount given in these equations. Adding this consideration, the total amount of methanol required can be estimated from the equation [29, 32, 34]

$$C_m = 2.47N_0 + 1.53N_1 + 0.87D_0 \quad (4)$$

where:

$C_m$  = required methanol concentration, mg/L

$N_0$  = initial nitrate concentration, mg/L

$N_1$  = initial nitrite concentration, mg/L

$D_0$  = initial dissolved oxygen concentration, mg/L

A methanol to nitrate-nitrogen mass ratio of 3.0, which results in about 90% denitrification yield, has been suggested as a design guideline [31].

A biological nitrogen removal system usually includes biological processes for nitrification, denitrification, and removal of carbonaceous nutrients. The system has a number of different process options, with various configurations of separation stages and hybrid processes and with the nitrification, denitrification, and biological oxygen demand removal arranged in different sequences. The denitrification process itself can also be divided into two categories: a suspended growth system in which denitrification is achieved in a mixed reactor, and an attached growth system in which denitrification is accomplished by microorganisms attached to growth media.

Several critical factors affect the design and operation of a biological denitrification system.

The denitrification rate is significantly reduced below pH 6.0 and above 8.0, with the highest rates occurring between 7.0 and 7.5. In other words, a neutral or slightly alkaline condition is optimal for denitrification [33].

The temperature effect on the growth of microorganisms for biological denitrification can be expressed as [30, 32]

$$r_m(T^{\circ}\text{C}) = r_m(20^{\circ}\text{C})M_T^{T-20} \quad (5)$$

where:

- $r_m(T^{\circ}\text{C})$  = maximum specific growth rate at  $T^{\circ}\text{C}$
- $r_m(20^{\circ}\text{C})$  = maximum specific growth rate at  $20^{\circ}\text{C}$
- $M_T$  = temperature coefficient, with a value of 1.07 for an attached growth system under typical operating conditions
- $T$  = temperature for denitrification, degrees Celsius.

Denitrification occurs between 0 and  $50^{\circ}\text{C}$ , with the highest rate occurring around  $40^{\circ}\text{C}$ .

High ammonia and calcium concentrations as well as a  $0.5 \text{ g/m}^3$  nickel concentration are reported to be inhibitory for denitrification [35]. Methanol does not inhibit the reaction up to a concentration of  $15 \text{ kg/m}^3$  of carbon content.

For the past two decades, a biological denitrification process has been mainly practiced in municipal wastewater treatment facilities in the United States and Japan. In the United States, plants are located in Washington, D.C., the Central Contra Costa Sanitary District, California, and Tampa, Florida. In Japan, there are more than 20 small-scale tertiary treatment plants using this technique. Because of the high cost of operations and the

increasing cost of methanol, alternative methods of nitrogen reduction, such as air stripping, chlorination, electrodialysis, reverse osmosis, and ion exchange, have been developed [30]. This could reduce demand for methanol in this application.

## 8.4

### Solvent/Cosolvent

#### 8.4.1

##### General Considerations

Solvent is designated as part of a solution that is in excess and is an organic compound used to dissolve, suspend, or change the physical properties of other materials. The purpose of solvents is to convert a substance into a form suitable for a particular use. The importance of the role of solvents is brought out most clearly by the fact that many substances exhibit their greatest usefulness when in solution [36, 37]. Generally, solvents are aromatic or aliphatic hydrocarbons, alcohols, aldehydes, ketones, amines, esters, ethers, glycols, glycol ethers, or alkyl or aromatic halides that boil at 75-220°C [36].

Methanol was one of the earliest organic solvents used in physical and chemical studies. Methanol, like other alcohols, is referred to as latent solvent, whose hidden solvent qualities are brought out by the addition of an active solvent. The presence of a latent solvent increases the tolerance of an active solvent for a nonsolvent. Therefore, latent solvent is also called an extender, because it increases the volume of a solution without decreasing the solvent power [37]. Some important physical properties for methanol as a solvent are listed in Table 3 [37, 40].

#### 8.4.2

##### Major Applications

The major applications for methanol as a solvent are in three areas: (1) it is used as a process solvent for extraction, washing, drying, and crystallization in various chemical processes; (2) it acts as a cosolvent in various formulations of paint and varnish removers; and (3) it is also used as a solvent in automobile wind-shield washer fluid for the removal of ice and insects. All these applications are mature, and their growth rates should not exceed the gross national product [2].

##### 8.4.2.1

##### Process Solvent in Chemical Manufacturing Processes

##### Separating and Purifying Acetylene [41, 44]

Currently, more than 85% of acetylene in the world is produced by the pyrolysis of natural gas or liquid hydrocarbons in various converters. The cracked gas produced in these converters has less than 10% in acetylene content. It contains predominantly a mixture of hydrogen, carbon monoxide, carbon dioxide, unreacted hydrocarbons, higher acetylenes, and inert gases.

The isolation of acetylene from the gas mixture is complicated because of the unstable and explosive nature of acetylene. To avoid operational hazards, most commercial processes employ absorption-desorption techniques using one or more selected solvents

to recover hydrocarbon-derived acetylene. Chilled methanol is the extraction agent chosen by Montecatini as the solvent in their acet-

Table 3 Physical Properties of Methanol

Physical properties	Numerical value
Autoignition temperature	385°C at 760 mm Hg
Boiling point	64.7°C at 760 mm Hg
Coefficient of expansion	0.00119 per °C at 20°C
Critical compressibility	0.224
Critical density	0.272 g/cm <sup>3</sup>
Critical pressure	81.12 kg/cm <sup>2</sup>
Critical temperature	240°C
Critical volume	3.6829 cm <sup>3</sup> /g
Density	0.7914 g/cm <sup>3</sup>
Dielectric constant	32.35 at 20°C
Dispersion	5.3 × 10 <sup>3</sup> at 20°C
Evaporation rate (ether = 1)	6.3
Explosive limits	
Lower	6.0 vol% in air
Higher	36.5 vol% in air
Flash point	
CC	12°C
OC	16°C
Heat of formation	
Liquid	57.012 kcal/g-mol at 25°C
Vapor	48.08 kcal/g-mol at 25°C
Heat of fusion	16.4 kcal/g-mol at 97°C
Heat of vaporization	8.44 kcal/g-mol at 64.7°C
Melting point	98°C
Molecular weight	32.04
Refractive index	1.3286 at 20°C
Solubility in water	Completely miscible at 20°C
Solubility of water in solvent	Completely miscible at 20°C
Surface tension	22.55 dyn/cm at 20°C
Vapor density (air = 1)	1.11
Vapor pressure	96.3 mm Hg at 20°C
Viscosity	0.5945 cp at 20°C

Source: From References 3740.

ylene recovery process. Furthermore, methanol is also used by Huels as the solvent to remove liquified higher acetylenes to prevent them from polymerizing and causing unnecessary complications when acetylene is used as a raw material in various chemical synthesis processes.

## Removing Acid Gas and Sulfur for Gas Purification [4549]

The Rectisol and Amisol processes, which were developed in Germany by Lürgi, are physical and physical-chemical absorption processes using organic solvents to remove acid gas and sulfur, respectively, from various gas streams. Both processes use methanol as the physical absorption solvent; the Amisol process also uses monoethanolamine (MEA) as the chemical absorber to improve the overall purification efficiency. The MEA used in the Amisol process is not pertinent to our topic. Only methanol used in the Rectisol process is discussed here, and the discussion is also applicable to the physical absorption by methanol used in the Amisol process.

Methanol is the preferred solvent because it has very high solubility for carbon dioxide and hydrogen sulfide at low temperature and elevated pressure, and they are readily released from the methanol when the pressure is reduced. The operating temperature and pressure of the absorber are about 0°C and 150 psig, respectively, and it is necessary to cool the process gas to the absorbing temperature.

The principal advantages claimed for the Rectisol process are as follows: (1) The energy requirement is lower than that required in the conventional monoethanolamine process for acid gas removal. This is because the solution is cooled by pressure reduction in the regeneration step, and the gas feed is refrigerated by efficient heat exchange with the outgoing purified and acid gas stream. (2) It is capable of removing all undesired impurities in a single process. (3) The purified gas obtained from the process has a very low water content. However, the Rectisol process also has several disadvantages: (1) the flow scheme is very complicated; (2) methanol has an appreciable vapor pressure even at low temperature, causing relatively high vaporization loss of the solvent; and (3) the purified gas contains more than 1% CO<sub>2</sub>, even after multistage treatments, final purification by more efficient methods is necessary if gases of low CO<sub>2</sub> concentration are required.

Currently, there are more than 100 commercial plants employing the Rectisol process for the treatment of synthesis gas or town gas streams to remove carbon dioxide and hydrogen sulfide.

## Poly(vinyl Alcohol) (PVA) Manufacture [5052]

Poly(vinyl alcohol), a polyhydroxy polymer, is the largest volume, synthetic water-soluble resin produced in the world. It is commercially produced by using poly(vinyl acetate) as a starting material by a base-catalyzed alcoholysis reaction. Methanol is the solvent chosen in the alcoholysis reaction. It is an important factor controlling the degree of polymerization. The alcoholysis reaction is carried out in a highly agitated slurry process; a fine precipitate forms



as the poly(vinyl acetate) converts to PVA. The product is then washed with methanol and is filtered and dried.

#### 8.4.2.2

##### Cosolvent in Paint and Varnish Removers [5358]

The main function of a paint and varnish remover is to remove all traces of the coating with minimal labor and time requirements. It should also leave the substrate intact and suitable for immediate reprocessing or refinishing. Because of the continuous improvement in paints, modern paints are more resistant to chemical removers. Therefore, an effective paint and varnish remover should possess the following characteristics: good stripping ability, lack of corrosiveness to substrate, freedom from noxious and toxic chemicals, long shelf life, low volatility, inertness to metals, and short waiting time for refinishing.

The most widely used removers are based on methylene chloride, which is the most versatile stripping agent commonly available. A typical remover based on methylene chloride has several components, including solvents, cosolvents, activators, corrosion inhibitors, evaporation retarders, thickeners, emulsifiers, and wetting agents. Methanol is the most widely used cosolvent, which has strong activating effect, adding the versatility of the remover in attacking coating as well as increasing the rate of stripping. Generally, a cosolvent is present at 510 wt% in a remover.

#### 8.4.2.3

##### Solvent in Automobile Windshield Washer Fluid [2, 6970]

One of the most substantial uses for methanol as a solvent is in automobile windshield washer fluid. The major function of the fluid is for ice and insect removal. It usually contains 1050% of methanol in water, depending upon the temperature in the area. However, because of the mild winters for the past few years in the United States, the largest single market globally, the demand for windshield washer fluid has been reduced.

### 8.5

#### Antifreeze

##### 8.5.1

##### Historical Development

Antifreeze is a material added to water-containing fluids to lower their freezing points. The largest single use for antifreeze is to protect internal-combustion engines against freezing and the resulting damage to the engine water jacket and radiator [7173]. Antifreeze also finds other small-volume uses in refrigeration systems, heat-transfer systems, hot-water heating systems, snow-melting systems, ice-skating rinks, automatic sprinklers, solar energy units, building air-conditioning systems, hydraulic systems, deicing fluids, water-based paints, pharmaceutical products, and freeze-drying apparatus.

Chemical antifreezes include

brines, alcohols, glycerols, and glycols. Since 1960, ethylene glycol has held the majority of the antifreeze market share because of its availability and superior performance. It has been produced in the United States since 1920 and in Europe for over 50 years [7173].

Methanol is a chemical that has a very good freezing point depression ability. It can depress the freezing point by 54.5°C for a 50/50 wt% methanol-water solution [74]. It also has good thermal properties and is inexpensive and readily available. Therefore, methanol, a by-product of wood distillation, was one of the most frequently used antifreezes before 1920. Synthetic methanol was first used as an antifreeze in the early 1930s. It was soon recognized as the best of the low-boiling antifreezes, being more efficient than its close competitor, ethanol. During the same period, prepackaged, formulated brand name antifreezes made from methanol were first introduced into the market. Except during World War II, methanol increased its market penetration to a high point in the early 1950s, after which it was replaced by ethylene glycol-based antifreezes and its market share gradually declined. By 1960, ethylene glycol-based antifreezes had more than 80% of the market share. Currently, methanol-based antifreezes are used in some stationary engines and are also required in older engines, which have a small share of the antifreeze market [7173].

### 8.5.2 Applications

The major use of methanol as an antifreeze is at present in desiccant-antifreeze applications for natural gas processing [7578]. The methanol-containing desiccant-antifreeze is used in both gas-collecting areas and natural gas pipelines. The amount of methanol used in this application depends on temperatures and climatic conditions. Methanol consumption for this use was about 202217 thousand t for North America in 1990 [75]. The future consumption for methanol in this area will depend essentially on the development of new natural gas reserves and gas-processing plants. Usually, the gas stream is countercurrently contacted with the liquid desiccant-antifreeze agent in a bubble tower to remove water from the gas and to vaporize some desiccant into the gas to prevent subsequent solid formation at low temperatures [78].

There are several other applications for methanol-based antifreezes:

1. Methanol acts as antifreeze in peroxide emulsions used in suspension polymerization of poly(vinyl chloride), poly(vinyl acetate), and acrylic-styrene resin. The methanol content is about 520 wt% in the emulsion [7983].
2. Low-concentration methanol was added as a deicer into gasoline and liquid hydrocarbons. Sales of this antifreeze also depend on the temperature and weather conditions [75, 8486].

3. Methanol is also added to the lines of artificial snow machines when they are not in use to prevent the machines and lines from freezing damage [75].
4. Methanol-containing antifreeze is also used as a snow and ice remover when it is sprayed on the road [87, 88].
5. Methanol is also used as low-temperature heat-transfer fluid in indirect refrigeration systems [89].

## 8.6

### Miscellaneous

There are several miscellaneous methanol applications that cannot be categorized in the previous sections and are described here.

Methanol is used as a reagent in some specialty chemical processes:

1. Synthesis of new o-chloro, p-chloro, and p-bromoanisoole-sulfonylamino acid derivatives, which are active against several microorganisms [90].
2. Preparation of pyridine compounds,  $\text{RCONHCH}(\text{CCL}_3)\text{ZR}_1$  ( $\text{R} = 3\text{- or }4\text{-pyridyl}$ ;  $\text{R}_1 = \text{alkyl, alkenyl, pyridyl, PhCH}_2\text{CH}_2$ , and so on;  $\text{Z} = \text{O or S}$ ), which can be used as bactericides [91].
3. Synthesis of substituted phenylthioamidines, which are useful as inhibitors of ADP and as antimicrobials [92].
4. Preparation of  $\alpha$ -acetylenic derivatives of  $\alpha$ -amine acids, which are useful as central nervous system stimulants, antibacterial agents, and irreversible inhibitors of glutamate decarboxylase [93].
5. Preparation of exo-3'4'-O-benzylidene-3''-dimethylchartreusin and its salts as antitumor and antibacterial agents [94].
6. Synthesis of 4-acetylamino-3-nitrobenzenesulfonylamino acid and dipeptide derivatives [95].
7. Preparation of 1,2,4-triazine-3-methanamines used as herbicides, insecticides, and fungicides [96].

Methanol is used in the steel industry [97]. Methanol has been proposed as a synthesis gas source in the direct reduction of iron or to sponge iron (containing 90% of Fe) by removing most of the oxygen at a temperature of about 850°C. Molten iron is not produced in this process but is formed in the conventional blast furnace route of iron core reduction. This process has gained popularity because it requires a smaller capital investment and produces a superior quality product than the traditional blast furnace route. Currently, natural gas is the primary reductant used, but methanol is considered when coal, natural gas, or fuel oil is not readily available at the iron ore mine mouth.

Methanol has also been considered as a substitute for reductant coke in blast furnaces. Methanol can be injected directly into the furnaces or cracked to syn-

thesis gas. In this application, methanol is competing against coke as well as fuel oil and natural gas. Prospects for methanol use in blast furnaces do not look favorable since blast furnace capacity is expanding primarily in energy-rich countries, where natural gas is probably the favored replacement for coke.

There has been intensive interest in transporting coal by slurry pipeline [98108] as an alternative to unit trains in the United States and Japan since early 1970s. There are several coal slurry pipelines operated in the United States, such as the Black Mesa Pipeline, Nevada Power, Energy Transportation Systems, Inc., and the Ohio Pipeline. These pipelines use water as transporting fluid. In the late 1970s, methanol was proposed as an alternative slurry medium for coal pipelines because (1) part of the coal could be converted to methanol at the mine mouth, ensuring the availability of slurry media; (2) converting coal to methanol can lower the average sulfur content of the slurry, which can reduce the air pollution problems encountered by most power plants; and (3) methanol has a higher load-carrying ability than water, and methanol itself can also be used as fuel. There are several disadvantages to the coal-methanol slurry: (1) a methanol slurry must be stored in a closed vessel compared with the agitated silos used for the coal-water slurry; (2) the separation of fine bone-dry coal from the methanol slurry must be handled in an inert atmosphere to avoid fire and explosion; and (3) 3 million ton/year of methanol is needed to transport 5 million ton/year of coal by a coal-methanol slurry pipeline. This requires a dedicated mine mouth methanol plant, which means it would require higher capital investment than a coal-water slurry pipeline of similar capacity.

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## 9

## Global Outlook: Supply, Demand, and Marketing

James R. Crocco  
Crocco & Associates, Inc., Houston, Texas

## 9.1

### Introduction

In 1991, tremendous optimism was held by the people involved in a number of industries around the globe concerning the prospects for oxygenated and reformulated gasolines mandated by the 1990 Clean Air Act Amendments in the United States. The first phase was to take place in November 1992, covering the 4 winter months in 39 metropolitan areas in the United States. The goal was to reduce seasonal carbon monoxide tail pipe emissions.

Beginning in 1991, the refining and gasoline industries started to stockpile large amounts of methyl tert-butyl ether (MTBE), which was to be the work-horse oxygenate, together with some ethyl tert-butyl ether and ethanol. This stockpiling took place for about 18 months, and as the first season began in late 1992, it became very apparent that there were high inventories of oxygenates available, and combined with new production scheduled to come on-line shortly, there would be sufficient quantities to carry through this first season. In a rush to obtain sufficient oxygenates, especially MTBE, the refining and gasoline industries were willing to pay practically any price for this gasoline ingredient.

It is rather apparent that methanol demand will follow the lead of its most significant derivative, MTBE. MTBE production will continue to increase at substantial levels for the foreseeable future.

The following is the current outlook for global methanol supply and demand divided into the major regions, estimated for 1992 with forecasts through 1995.

## 9.2

### Regional Outlook

#### 9.2.1

##### North America

Formaldehyde production in the United States in 1992 registered a 9% increase versus the previous year (Table 1 and Fig. 1). Of course, formaldehyde production had been on the decline during the recession. It is not believed that 1992 represented a normal year for formaldehyde since a large amount of home building and repair was necessitated by Hurricane Andrew in August and also by numerous tornadoes and hailstorms later in the year. Methanol use for gasoline blending (M85) and other direct fuel uses is expected to increase in the United States as a large number of new, flexible-fueled vehicles come into the market, especially in California. It is believed that by 1995 there could be more than 20,000 of these vehicles. Also, "neat" or 100% methanol is being used increasingly as a replacement for diesel fuel in buses, and it is estimated that by the middle of this decade the city of Los Angeles alone could have well over 500 such units.

Table 1 Forecasted North American Methanol Supply and Demand Balance (Hundreds t)

Demand	Estimated, 1992	Forecast		
		1993	1994	1995
Formaldehyde	1680	1714	1748	1783
Dimethyl terephthalate	201	203	205	207
Acetic acid	600	600	600	600
MTBE	1950	2850	3750	4700
Methyl methacrylate	195	198	198	198
Gasoline, fuels	17	40	78	130
Solvents	282	290	299	307
Others	1157	1176	1191	1210
Total demand	6082	7071	8069	9135
Nameplate production capacity	7644	7654	9154	9154
Capacity at 90%	6880	6889	8239	8239
Forecasted surplus/(shortage) at 90%	798	(182)	170	(896)

Source: From 1992 Methanol Annual.

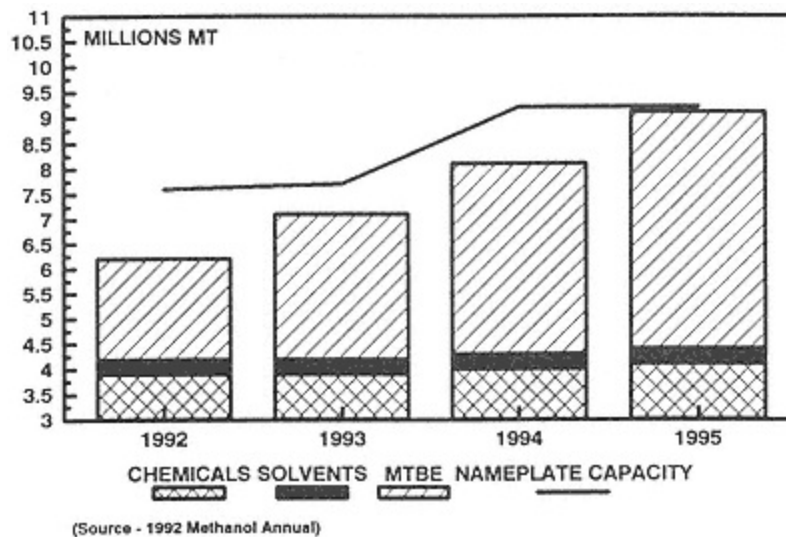


Figure 1

Forecasted North American methanol demand by product group.

### 9.2.2 Western Europe

In the forecast shown in Table 2 and Figure 2, we were somewhat generous for Western European formaldehyde production, increasing it at about 4% for the total 3 year period. We are assuming that economic conditions will improve in some of the larger Western European countries, such as Germany, and that some of the other countries will experience stronger economic growth. The large increase in methanol demand for acetic acid between 1994 and 1995 assumes that Hoechst will complete construction of a new, large acetic acid plant in Germany in 1994 and experience full production the following year. It is very possible, however, that this facility could be delayed to outside the forecast period. Otherwise, methanol demand for other uses falls in line with general expectations.

### 9.2.3 Far East and Asia

This region of the world is still experiencing strong economic growth, at least compared with other regions (Table 3 and Fig. 3). Therefore, we are somewhat optimistic on continued methanol demand for the production of formaldehyde and also dimethyl terephthalate. There will be some acetic acid production ex-

Table 2 Forecasted Western Europe Methanol Supply and Demand Balance (Hundreds t)

Demand	Estimated, 1992	Forecast		
		1993	1994	1995
Formaldehyde	2411	2435	2469	2512
Dimethyl terephthalate	92	93	93	93
Acetic acid	365	365	365	575
MTBE	953	1003	1013	1028
Methyl methacrylate	124	174	174	174
Gasoline, fuels	50	50	50	50
Solvents	167	172	174	179
Others	1007	1022	1040	1056
Total demand	5169	5314	5378	5667
Nameplate production capacity	2970	2970	2970	2970
Nameplate at 90%	2673	2673	2673	2673
Forecasted surplus/(shortage) at 90% (importability)	(2496)	(2641)	(2705)	(2994)

Source: From 1992 Methanol Annual.

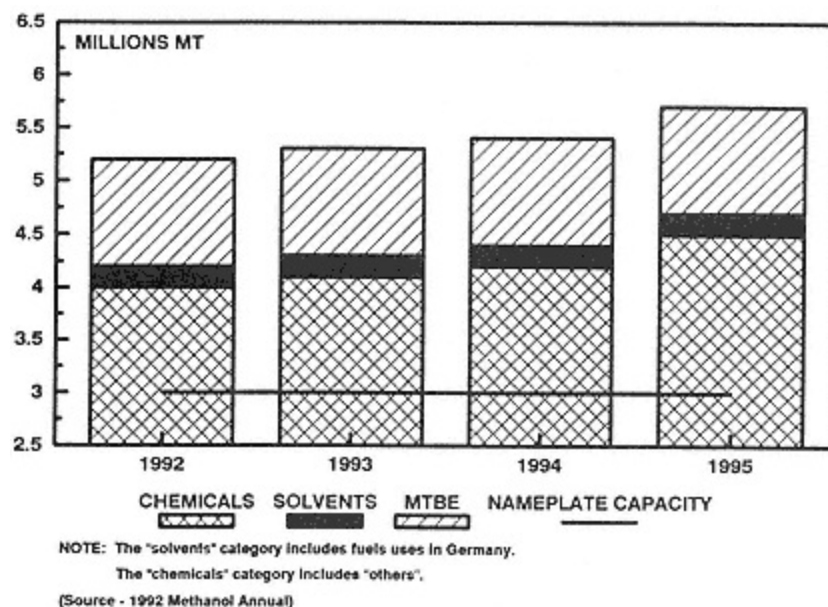


Figure 2  
Forecasted Western European methanol demand by product group.

Table 3 Forecasted Far East and Asia Methanol Supply and Demand Balance (Hundreds T)<sup>a</sup>

Demand	Estimated, 1992	Forecast		
		1993	1994	1995
Formaldehyde	1798	1816	1912	1961
Dimethyl terephthalate	221	224	230	235
Acetic acid	270	358	380	385
MTBE	231	386	420	430
Methyl methacrylate	152	197	210	235
Gasoline, fuels	183	196	201	206
Solvents	183	196	201	206
Others	1079	1149	1144	1173
Total demand	3934	4326	4497	4625
Nameplate production capacity	3108	3358	3538	3538
Nameplate at 90%	2797	3022	3184	3184
Forecasted surplus/(shortage) at 90% (importability)	(1137)	(1304)	(1313)	(1441)

<sup>a</sup> There are current supply contracts to the Far East from Canada and Saudi Arabia for about 1.1 million ton methanol per year. The Far East is in fact a net methanol exporter for the moment.

Source: From 1992 Methanol Annual.

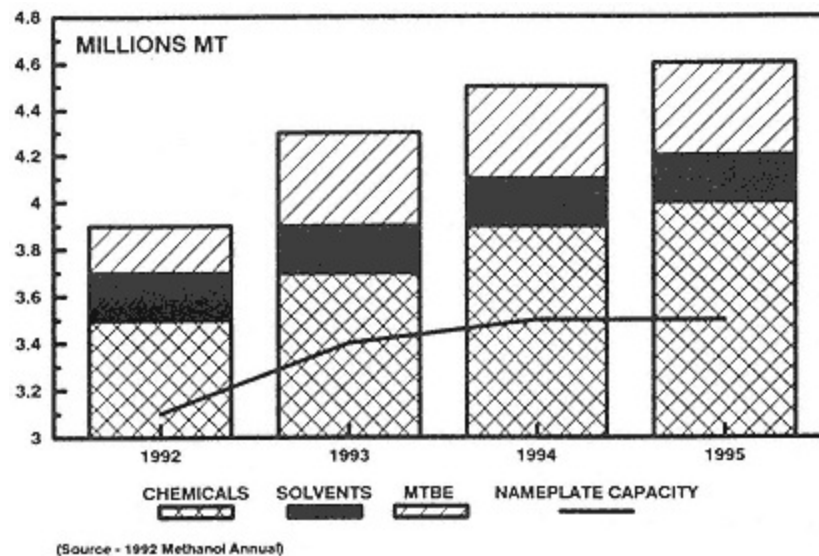


Figure 3  
Forecasted Far East and Asia methanol demand by product group.

pansion in the region, primarily for use as a process solvent for the production of purified terephthalic acid, and MTBE production is expected to increase principally in Japan and Korea.

#### 9.2.4

##### South America

The big impact on methanol demand in South America has been the fairly new requirement for blending into gasoline in Brazil. In late 1989, Brazil started to import large quantities of methanol as a replacement for fuel ethanol. The world sugar market became rather strong, and Brazilian sugar growers preferred to concentrate on the global market at higher returns than provide feedstock for fuel ethanol production to power the 4 million alcohol-fueled vehicles. However, there are strong indications that this fuel requirement is dwindling in the face of lower world sugar prices, making ethanol feedstocks more readily available. Otherwise, we anticipate that forecasted (Table 4 and Fig. 4) South American methanol demand for the study period will remain at more or less traditional levels, except for the possibility of a new MTBE plant coming on-line in Trinidad in 1995. This facility could also be postponed to outside the forecast period.

Table 4 Forecasted South American Methanol Supply and Demand Balance (Hundreds t)

Demand	Estimated, 1992	Forecast		
		1993	1994	1995
Formaldehyde	197	201	205	211
Dimethyl terephthalate	26	26	26	26
MTBE	247	247	247	297
Methyl methacrylate	8	8	8	8
Gasoline, fuels	450	400	300	200
Solvents	25	26	28	29
Others	36	36	39	40
Total demand	989	944	853	911
Nameplate production capacity	1529	1804	3014	3114
Capacity at 90%	1376	1624	2713	2803
Forecasted surplus/(shortage) at 90% (exportability)	387	680	1860	1892

Source: From 1992 Methanol Annual.

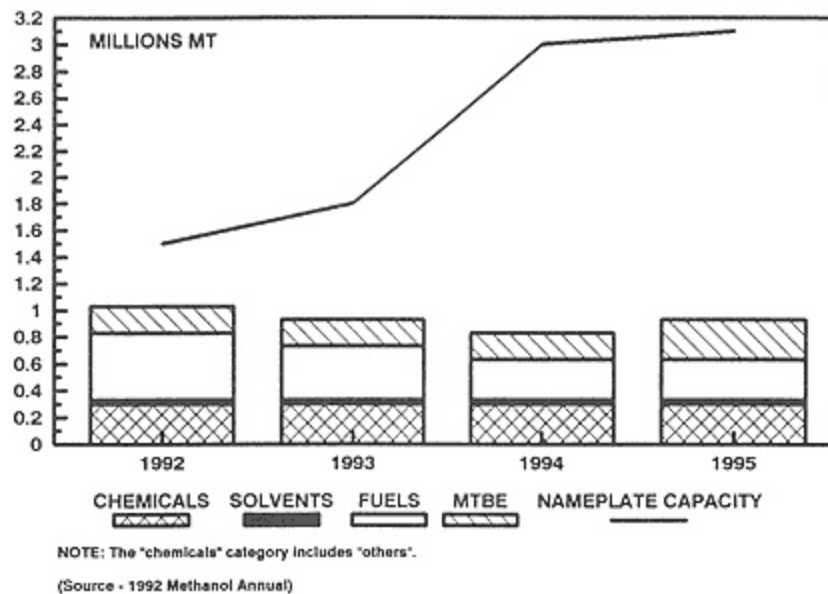


Figure 4  
Forecasted South American methanol demand by product group.

### 9.2.5 Middle East and Africa

A number of additional MTBE plants are scheduled to be built in Saudi Arabia and elsewhere around the Arabian Gulf by the middle of this decade. If they all materialize, then methanol demand for this outlet will grow quite dramatically, reducing export ability from the region. However, our forecast only goes to the year 1995 and includes those projects we consider most realistic (Table 5 and Fig. 5). Note that our supply forecast is based on 90% of nameplate production for the region. It is well known that many, if not most, of the existing methanol-producing facilities in the Middle East are able to operate above their nameplate capacity, and in fact, some of them have already been rerated upward to allow for some of this increased efficiency. Therefore, it is very possible that the Middle East and Africa can and will have additional methanol export ability to that indicated. On the other hand, because of increased MTBE capability in the region, we still anticipate reduced methanol export availability overall.

Table 5 Forecasted Middle East and Africa Methanol Supply and Demand Balance (Hundreds t)

Demand	Estimated, 1992	Forecast		
		1993	1994	1995
Formaldehyde	197	200	201	202
Dimethyl terephthalate	12	12	12	13
MTBE	191	191	573	964
Solvents	37	37	39	39
Others	81	82	85	86
Total demand	518	522	910	1304
Nameplate production capacity	3406	3406	3406	4066
Nameplate at 90%	3065	3065	3065	3659
Forecasted surplus/(shortage) at 90% (exportability)	2547	2543	2155	2355

Source: From 1992 Methanol Annual.

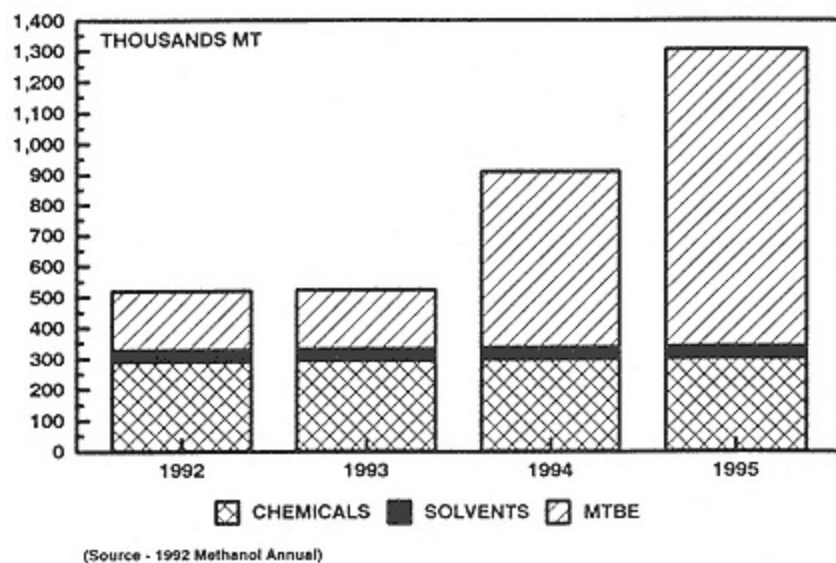


Figure 5  
Forecasted Middle East and Africa methanol demand by product group.



## 9.2.6

### Central and Eastern Europe

Between 1990 and 1991 we factored in a decrease in total methanol demand for Central and Eastern Europe of about 10% (Table 6 and Fig. 6). It can be seen that we anticipate only a very small increase in overall methanol demand from 1992 to 1995. Actually, this could prove to be somewhat on the optimistic side, since many of these countries are still experiencing serious economic downturns. A number of new methanol-derivative facilities are planned, such as MTBE, but the ability of these countries to arrange secure financing is very doubtful, at least at this time. Also, there remain large amounts of methanol feedstocks in Siberia, but the ability to finance expanded methanol production is also a serious hurdle. We understand that the one methanol-producing facility in the Ukraine, with a nameplate capacity of 500,000 t per year, may be closed permanently because of the high cost of feedstock originating in Siberia.

## 9.2.7

### Worldwide

Total global methanol demand for the study period from 1992 to 1995 is expected to increase by approximately 26%, or 8% per year (Table 7 and Figs. 79). On the surface, this appears rather strong. However, it is led by anticipated dramatic increases in methanol demand for the production of MTBE. This

Table 6 Forecasted Central and Eastern Europe Methanol Supply and Demand Balance (Hundreds t)

Demand	Estimated, 1992	Forecast		
		1993	1994	1995
Formaldehyde	1059	1076	1094	1113
Dimethyl terephthalate	125	125	125	125
Acetic acid	172	172	172	172
MTBE	363	363	363	363
Solvents	55	55	55	53
Others	629	641	653	663
Total demand	2403	2432	2462	2489
Nameplate production capacity	4980	4980	4980	4980
Nameplate at 90%	4482	4482	4482	4482
Forecasted surplus/(shortage) at 90%	2079	2050	2020	1993

Source: From 1992 Methanol Annual.

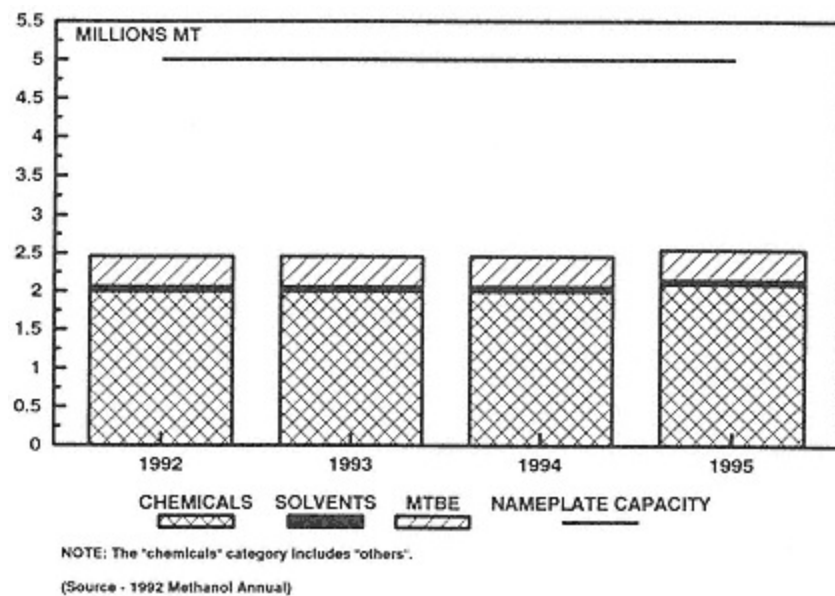


Figure 6  
Forecasted Central and Eastern European methanol demand by product group.

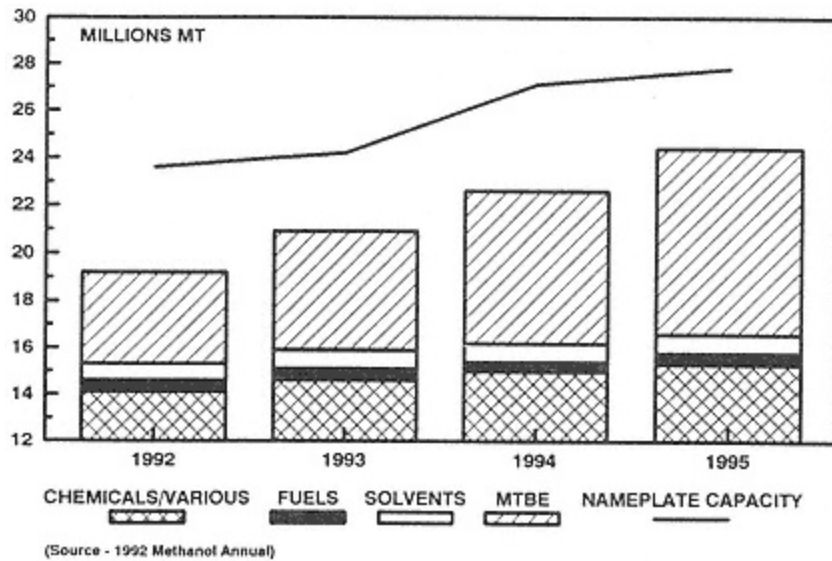


Figure 7  
Forecasted world methanol demand by product group.

Table 7 Forecasted World Methanol Supply and Demand Balance (Hundreds t)

Demand	Estimated, 1992	Forecast		
		1993	1994	1995
Formaldehyde	7,342	7,442	7,629	7,782
Dimethyl terephthalate	677	683	691	699
Acetic acid	1,407	1,495	1,517	1,732
MTBE	3,935	5,040	6,366	7,782
Methyl methacrylate	479	577	590	615
Gasoline, fuels	517	490	428	480
Solvents	749	776	796	813
Others	4,027	4,149	4,372	4,228
Nontabulated countries	210	215	220	225
Total demand	19,343	20,867	22,609	24,356
Nameplate production capacity	23,637	24,172	27,062	27,822
Capacity at 90%	21,273	21,755	24,356	25,040
% Utilization at nameplate	81.8	86.3	83.5	87.5
% Utilization at 90% nameplate	90.9	95.9	92.8	97.3

Source: From 1992 Methanol Annual.

particular demand alone is expected to grow by a total of approximately 98% or about 25% or more per year. Other derivative growth factors are expected for formaldehyde, for a total of approximately 6%, acetic acid for a growth of about 23%, and methyl methacrylate for about 28%, although starting from a low base. Gasoline and fuels outlets for methanol are expected to expand dramatically in the United States (from a low base), but declines are anticipated for Brazil, resulting in an overall decrease in methanol demand for fuels uses of about 7%. All other chemical end uses are expected to perform according to traditional patterns.

We now review the status of current global methanol-producing capability as of the end of 1992 (Table 8) and the possibility or probability of new capacity coming on-line within the next 34 years (Fig. 10).

We categorize the potential and probability of future methanol-producing capacity as follows [1]:

Category A refers to plants currently under construction or those that appear to have finalized all important details and are expected to begin construction very soon (Table 9).

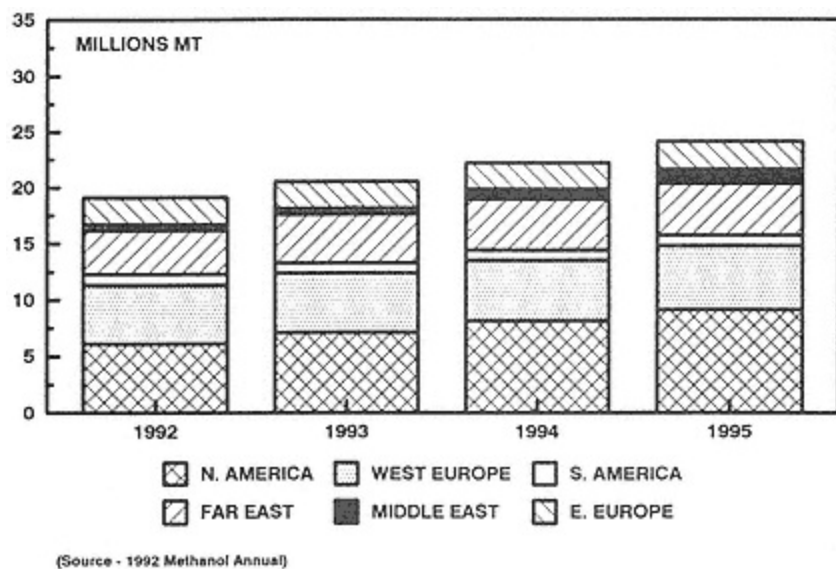


Figure 8  
Forecasted world methanol demand by region.

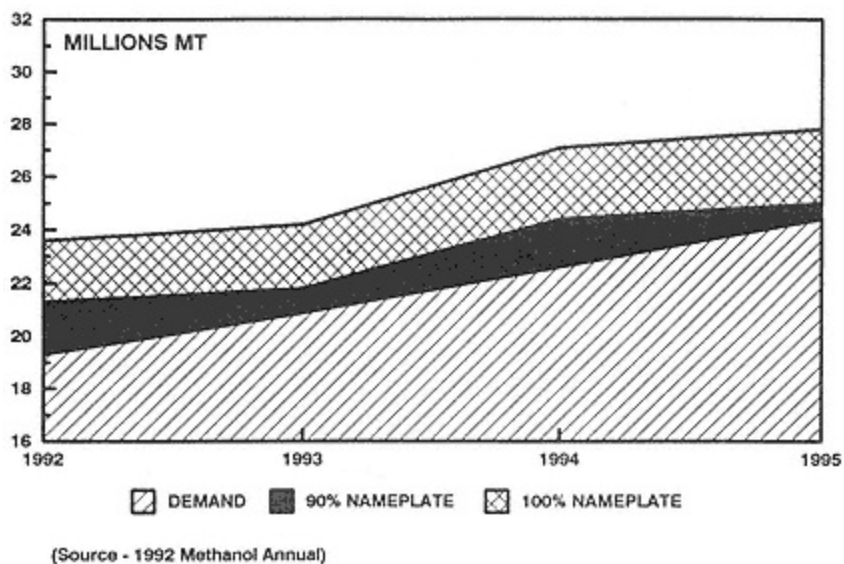


Figure 9  
Forecasted world methanol supply and demand balance.

Table 8 Estimated 1992 World Methanol Production Capacity

Country	Company	Feedstock/process	Nameplate capacity (hundreds t)
USA	Air Products	NG/ICI	180
	Ashland	NG/Lurgi	390
	Beaumont Methanol	NG/Lurgi	850
	Borden	NG/ICI	600
	Coastal	NG/ICI	80
	Enron	NG/Lurgi	375
	Georgia Gulf	NG/ICI	420
	Hoechst Celanese	NG/Lurgi	550
	Lyondell	NG/ICI	680
	Quantum	Resid/Lurgi	600
	Sand Creek	NG/Lurgi	80
	Tennessee Eastman	Coal/Lurgi	195
	Texaco	NG/Lurgi	300
Canada	Celanese	NG/ICI	750
	Methanex	NG/ICI	518
	Novacor	NG/ICI	900
Mexico	PEMEX	NG/Lurgi	172
Germany	BASF	OG/BASF	240
	DEA	Resid/Lurgi	450
	Leunawerke	Resid/Lurgi	660
	Veba	Resid/Lurgi	260
Italy	OMV	NG	120
Netherlands	Methanor	NG/ICI	740
UK	ICI	NG/ICI	500
Burma	State	NG/Lurgi	150
China	State, various	Various	700
India	Assam	OG/MGC	32
	Deepak	Naphtha/ICI	100
	FCI	Fuel oil/Haldor-Topsøe	40
	Gujarat	NG/Lurgi	100
	Pertamina	NG/Lurgi	330
Iran	State	NG/Dutch	100
Japan	MGC	NG/MGC	270
Malaysia	Petronas	NG/Lurgi	660
New Zealand	Fletcher Challenge D-1	NG/ICI	430
	Petrocorp D-2	NG/ICI-Davy (MTG)	450

(continued)

## Table 8 Continued

Table 8 Estimated 1992 World Methanol Production Capacity

Country	Company	Feedstock/process <sup>a</sup>	Nameplate capacity (hundreds t)
Argentina	Casco	NG/ICI	22
	Atanor	NG	15
	Resinfor	NG	50
Brazil	Alba	RG	32
	Metanol	NG/ICI	70
	Prosint	RG	118
Chile	Cape Horn	NG/Kellogg	750
Trinidad	TTMC	NG/ICI	450
Algeria	Almer	NG/ICI	110
Bahrain	Gulf PIC	NG/ICI	425
Israel	Dor	OG	55
Libya	SIRTE	NG/ICI	660
Saudi Arabia	Ar-Razi Nos. 1 and 2	NG/MGC	1,320
	Ibn-Sina	NG/ICI	770
South Africa	AECI	Coal/UHDE	20
	SASOL	Coal	6
Bulgaria	State		60
Czechoslovakia	State		100
Poland	State	NG/OG	200
Romania	State	NG/ICI	400
CIS	State	NG/ICI	1,650
	State	Various	2,140
Yugoslavia	State/Zagreb	NG/Lürgi	180
	MSK/Kikinda	NG/ICI	200
Total world			23,775

<sup>a</sup> NG, Resid, OG, RG.

Source: From 1992 Methanol Annual.

Category B are those facilities that have progressed well into the engineering stage, that appear to have financing arranged, and that, in our opinion, are good possibilities for completion (Table 10).

Category C are those plants that are only under consideration and/or in the initial stage of planning and have not progressed into the final engineering stage or arranged financing (Table 11).

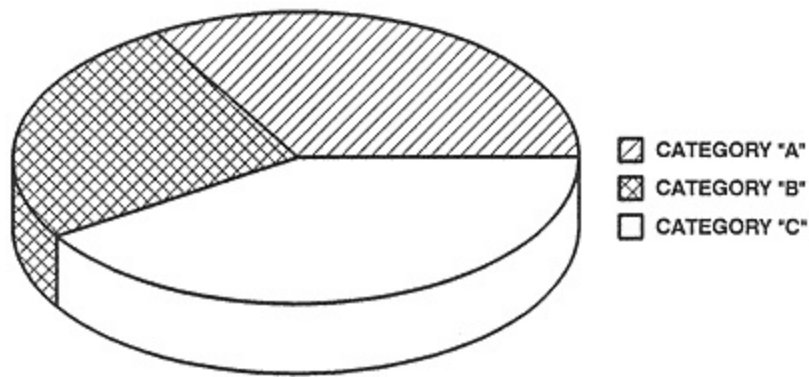


Figure 10  
Forecasted global methanol production outlook.

### 9.3 Major Traditional Methanol Derivatives

The major traditional derivatives for methanol are described here.

Formaldehyde is a very traditional outlet for methanol. It is used in resins for building materials, engineering plastics, and many other applications. Historically, global methanol demand for formaldehyde was very close to or above 50%, but this ratio is decreasing because of the advent of other products. Increases in formaldehyde demand generally kept pace with economic development in various regions, but in recent years this condition has changed somewhat. Although increases in formaldehyde production in the United States and Western Europe appear to keep pace with traditional patterns, in the Far East and Asia formaldehyde production is expanding at higher levels because of the strong wood products industry in that region of the world. Concern about the toxicity or carcinogenic effects of formaldehyde have stabilized production in some regions, whereas in others there appears to be only minimal concern, for example in the Far East. Overall, in our opinion, the use of methanol for the production of formaldehyde will continue to increase according to the global patterns of the past, or at about 2% per year depending on the location and economic conditions. However, should there be any serious recessions in the world, housing production and therefore formaldehyde use would be reduced, at least for that significant outlet.

The carbonylation of methanol to produce acetic acid was developed in the 1970s by Monsanto, and BP Chemicals has now taken over this process and development. It is the most efficient route to acetic acid, and because of this it

Table 9 Category "A" Methanol Plants

Country	Company	Location	Quantity (hundreds t/year)	Status
USA	Fortier	Louisiana	570	Converting American Cyanamid ammonia plant, 1994
	Ashland	Louisiana	70	Debottleneck 1993
	Georgia Gulf	Lousiana	90	Debottleneck 1994
	Terra Meth	California	10	Based on municipal waste, 1994
	Terra Int.	Oklahoma	150	Preliminary plans
Canada	Novacor	Alberta	100	Debottleneck 1994
Trinidad	Caribbean	Point Lisas	550	Under construction 1993
	TTMC	Point Lisas	500	New 1995
Venezuela	Metor/Japanese	Jose	730	Under construction 1994
Argentina	Resinfors		100	Debottleneck 1995
Australia	BHP/ICI	Near Melbourne	50	BHP/ICI entered into an arrangement to build a small methanol plant to prove new technology; this stalled for awhile but it is now proceeding
Norway	Statoil	West Coast	830	Engineering 1996
New Zealand	Fletcher Challenge Methanol	Waitara	450	Additional distillation 1994
Chile	Cape Horn	Punta Arenas	250	Debottleneck 1995
Qatar	Total/Int. Octane		660	Proceeding 1996
Total			5110	



Table 10 Category "B" Methanol Plants

Country	Company	Location	Quantity (hundreds t/year)	Status
USA	Various	Various	300	We are aware of a number of plans in various stages to construct some small methanol plants in nontraditional locations, and some are based on unique feedstocks
Venezuela	Ecofuel/Pequiven	Jose	660	Still alive/proceeding
Qatar	Penspen		660	Proceeding
Nigeria	Penspen		750	Planned/proceeding
	Mobil		850	Planned
	Standard Petrochemicals/MG	700	Planned	
Total			3920	

Table 11 Category "C" Methanol Plants<sup>a</sup>

Country	Company	Location	Quantity (hundreds t/year)	Status
USA	Various	Various	1000	Various plans for a number of facilities including one worldscale attached to a steel mill
Venezuela	Mitsui/Eastman	Jose	700	On hold
Argentina	Petroquimica Austral	Tierra del Fuego	700	Has been discussed for more than 10 years
China			200	Some preliminary plans
India			200	Some preliminary plans
Indonesia	PT Humpuss	Bontang	700	Doubtful at this point because of high infrastructure cost and feedstock value
	Pertamina	Sulawesi	700	Doubtful at this time because of high infrastructure costs
Algeria	Total/Sonatrach		700	Preliminary plans hampered by political situation
Iran	Galadari		700	Tied into an MTBE plant; preliminary
Saudi Arabia	SABIC/Ar-Razi	Al-Jubail	700	Preliminary plans
Total			6300	

<sup>a</sup> There are some preliminary plans for additional methanol-producing capacity in such countries as Mexico, Brazil, Angola, Colombia, and practically any other country that has natural or associated gas. We do not include them here because they have not, in our opinion, progressed beyond the initial idea stage and/or are looking for partners.

is our opinion that methanol demand for the production of acetic acid is rather recession proof. If there is any future need to rationalize the acetic acid industry, the first plants to be shut down would probably be those that are less efficient than the methanol process. A new world-scale acetic acid facility came online a few years ago in the United Kingdom. We know of other smaller facilities that may come on-stream in the next few years in the former Soviet Union and one that recently started up in South Korea. Hoechst AG intends to build a new methanol-based acetic acid facility in Frankfurt, Germany, which could be on-stream about 1995/1996 and would have the capability of consuming an additional approximate 240,000 t/year of methanol. Also, later in this decade, Tennessee Eastman may expand their acetic anhydride and acetic acid production in Kingsport, Tennessee. In addition, Hoechst Celanese expects to expand their acetic acid production at Bayport, Texas in a few years. Some other small acetic acid production could come on-line in other parts of the world to supply expanded production of purified terephthalic acid. The acetic acid industry is comparatively small, which makes it much more stable and sensitive to supply-demand balances. Therefore, we expect longer term acetic acid production to keep pace with expanded demand throughout the world, but there could be a surplus of acetic acid in the middle of the 1990s and the full potential of this methanol derivative may not be felt until later.

Undoubtedly, MTBE is the fastest growing petrochemical in the world. Its primary use is only as a blending component for gasoline. Pioneers in the field were Huels in Germany and Snamprogetti in Italy, but many other technologies have been developed. The demand for MTBE in the United States increases very dramatically as lead phasedown in gasoline reaches almost 100%. Those producers of more traditional octanes, such as toluene, tend to retain their products for their own gasoline pool, taking octane off the merchant market. This deficiency is now being supplied by MTBE. However, at least in the United States, MTBE is not viewed any longer as an octane ingredient or booster. It has now become a very integral part of a clean air strategy because by blending up to 15% of MTBE into gasoline, total aromatics, benzene, and olefins can be decreased along with Reid vapor pressure. The oxygen content of gasoline can be increased to allow more efficient combustion, especially at high altitudes and in serious air quality nonattainment regions of the country. This makes MTBE much more valuable as an oxygen booster in gasoline than as an octane component in the United States. Although Western Europe is somewhat behind the United States in lead phasedown and lead-free gasoline, these developments are now occurring in that region of the world in significant proportions to increase greatly the future demand for octane and, therefore, MTBE. We forecast greatly increased methanol demand for MTBE during the next 5 years.

throughout the world, although the increase may level off somewhat later. New plants are being constructed and planned for almost any region that has sufficient availability of the cofeedstock, isobutylene. Large world-scale plants are being considered, which will use field butanes to produce isobutylene, such as the first facility in Saudi Arabia and the one in Venezuela that started up early in 1991. Additional dehydro MTBE plants will be coming on in 1992 and thereafter. In our opinion, by the middle of this decade, MTBE demand (not production) in the United States alone could reach 2025 million t/year. This quantity equates to a methanol consumption of 7.09.0 million t/year, or the equivalent of 1013 worldscale methanol plants. However, we expect some of the future potential MTBE producers, especially those located in more remote regions, to consider building either small or world-scale methanol plants within their facilities to ensure the alcohol feedstock and also potentially to supply incremental quantities to world markets.

Formaldehyde, acetic acid, and MTBE represent almost two-thirds of methanol demand worldwide. The balance of methanol demand is for various other chemicals, such as DMT, methyl methacrylates, chloromethane, and methyl amines, and also for antifreeze, dehydration, and solvent purposes. Each one of these outlets is relatively individually small; therefore we do not review them here. In general, methanol demand for these various chemicals and solvents uses will expand with regional economic developments, and this is indicated in our methanol demand tables.

We are not at all enthusiastic or optimistic about significant expanded methanol demand for direct fuels uses any time in the foreseeable future. Major proponents for the direct use of methanol as a fuel are currently in the State of California and some other smaller, isolated locations. The drive is motivated by political and environmental reasons to reduce air pollution. However, studies are still being made concerning the production of formaldehyde emissions when using methanol as a fuel for internal combustion engines, which may not be an acceptable trade-off. In fact, even the politicians and environmentalists in the State of California appear to be changing their direction away from methanol (which requires an elaborate and expensive fuel distribution infrastructure) and toward more easily accessible alternative fuels, such as compressed natural gas, and also reformulated or clean gasolines, which could theoretically reach almost 100% of the automobile population in a relatively short period of time. Building methanol-fueled vehicles would take a considerable amount of time and investment. Even in Western Europe, where methanol demand reached about 700,00 ton per year in the mid-1980s for blending into gasoline, this practice has dropped off considerably. The reason was the drastic decline in crude oil values in late 1985 and early 1986, which reduced the value of gasoline com-

pared with that of methanol. Methanol has always been considered an inexpensive gasoline extender, not an octane booster, and unless methanol is priced at maximum 60% of wholesale gasoline, it will not find an economic outlet in gasoline blending. Many of the gasoline distribution systems have now become wet, and there are technical and logistical drawbacks to reviving the practice. Because of the added expense of preparing distribution systems to accommodate gasoline containing methanol, we expect only very limited additional methanol blending at best unless crude oil, and therefore gasoline values, rise dramatically from current levels. In our opinion, when crude oil reaches a sustained \$30 or more per barrel the equivalent price of gasoline will make methanol blending attractive once more. For methanol use as a direct fuel, crude oil values would have to reach a sustained \$40 or more per barrel.

In summation, except for acetic acid and MTBE, we do not anticipate methanol demand for the more traditional outlets in chemicals and solvents uses to grow at significant levels during the study period. For the most part, the growth will be based on regional and country gross national (domestic) product. In the short term (during the next 5 years), we foresee additional acetic acid production capability springing up around the world, but questions remain concerning the ability of these new plants to produce at maximum levels because of market saturation. It is possible, however, that lower cost acetic acid production for methanol could rationalize some of the more traditional production from other feedstocks, but this will not occur overnight. As mentioned previously, MTBE remains the single most attractive demand-growth methanol derivative, at least for the balance of this decade.

## 9.4

### Methanol Future Potential Chemical Applications

The present chemical outlets for methanol in the more traditional regions are rather well known and are even reaching maturity, as for formaldehyde and acetic acid to a lesser degree. There are some distinct chemical uses, however, that could provide new and alternative outlets for methanol somewhere in the more distant future. Producing various chemicals from feedstock methanol can result in a better value-added ratio than using methanol for fuels. Listed here are some of the routes to higher valued chemical products:

#### Methanol

Carbonylation: acetic acid, acetic anhydride, methyl acetate, methyl formate

Reductive carbonylation: acetaldehyde, ethanol, ethyl acetate, ethylidene diacetate

Oxidative carbonylation: dimethyl carbonate, dimethyl oxalate

## Formaldehyde

Carbonylation: glycolic acid, glycolic acid esters

Reductive carbonylation: ethylene glycol, glycolaldehyde

Of these, acetic acid synthesis from methanol is at present a commercial reality, as is acetic anhydride produced by Tennessee Eastman in the United States from coal-based methanol.

Some of the other products just listed, such as ethanol, ethyl acetate, and ethylene glycol, can be considered commodity chemicals. Competition is strong in these products since new plants based on traditional olefin feedstocks have been built in energy-rich countries and there are plans for expansion. For new technology to justify replacing the old, it must provide "shutdown" economics for low-growth products, but we do not predict C<sub>1</sub> chemistry will be able to do this in at least 10 years or more.

Toluene can be reached with methanol over a type X zeolite containing cesium and boron to produce a styrene and ethylbenzene mixture that can be further processed to specification styrene monomer. However, we do not anticipate this process developing in the near future because at present styrene monomer capacity based on the traditional feedstocks of ethylene and benzene at current lower feedstock costs.

The chemistry to produce aromatics from methanol is rather well known. In one process, light olefins are converted from methanol over an acid catalyst, which are then oligomerized and cyclized to aromatics. The Mobil methanol-to-gasoline (MTG) process has a special feature that limits the growth to a C<sub>10</sub> by using synthetic ZSM-5 zeolite, placing the product in the gasoline range. This step also prevents the formation of aromatic coke precursors. A commercial MTG plant is in operation in New Zealand and has the ability to supply 33% of that country's gasoline demand, although at high production costs relative to the availability of cheaper gasoline on the world market. Although this plant is a technical success, because of the high losses incurred by producing synthetic gasoline there are additional plans to "clean up" some of the commercial-grade methanol feedstock and place it on the world chemical market.

We do not anticipate significant technical developments for new methanol-based chemicals in this century. The primary constraint is stabilized, more traditional raw material prices, especially ethylene, and slow growth in end-product demand. A significant increase in petroleum prices, however, combined with a more normal growth pattern in end uses, could change this scenario sometime in the more distant future. The desire to obtain better value-added products than for fuels, better catalysts and new technology, and more research and development will greatly assist the new chemical outlets for methanol. We

could very well be standing on the threshold of an exciting revolution in C1 chemistry.

## 9.5

### Single-Cell Protein Manufacture

Methanol can be used as a carbon source for the production of single-cell protein (SCP) for use as an animal feed supplement. The SCP process nurtures a living organism by using methanol (carbon), ammonia (nitrogen), and air (oxygen). The end result is a powdered or granular product that can be used to feed cattle, pigs, poultry, fish, and so on, in concentrations of 830% SCP (depending on the application) mixed or formulated with other, more conventional feeds. Some of the more conventional feeds are soya, fish meal, and concentrated grains. Methanol-based SCP results in a high nucleic acid content, which makes it unfit for human consumption, although some technology could solve this problem in the future.

The only large-scale commercial SCP facility in the Western countries using methanol as a substrate was the 50,000 ton per year plant in England operated by ICI, but this plant shut down for economic reasons. Phillips Petroleum has a SCP technology called Provesteen, with a protein content of about 62%, and there are reports they are planning to build a 10,000 t/year SCP plant in China (People's Republic). Reports indicate the former Soviet Union at present has a SCP capacity of 1.0 million ton, but using a low-grade carbohydrate base and normal paraffins, which result in protein contents of 53 and 60%, respectively. SCP based on methanol via the ICI process produces a protein content of 72%.

SCP production has unlimited worldwide potential under proper conditions. By producing an animal feed supplement (and extender), more conventional grains and feeds can be displaced for human consumption. It requires 1.62.0 ton methanol to produce 1.0 ton SCP, and a large market for methanol could be on the horizon, especially in the less developed and/or energy-rich countries.

There are two major problems facing the expansion of SCP production from methanol at this time. The first is the continued availability of traditional feeds at reasonable prices, and the second could be the relatively high cost of natural gas (i.e., methanol) in the more developed nations.

There are many dislocations associated with grain production throughout the world, mostly because of weather conditions and fuel and fertilizer costs. As energy values increase, which they are certain to do in time, grain will be more expensive. Also, there are only so many fish in the sea, even if they are a renewable resource. The combination of weather variances, higher energy costs, and lesser yields from the oceans could promote SCP expansions.

At present, it is not commercially practical to produce SCP from methanol, even on a large scale, at least not in the West. Other SCP-manufacturing plans have been mentioned for Saudi Arabia, Malaysia, and Indonesia. Turning natural gas into an animal food supplement via methanol may prove to be an interesting prospect sometime in the future.

## 9.6

### Sewage Treatment

Methanol can be used for dinitrification of wastewater in the tertiary stage of treatment. It is used as a carbon source to grow bacteria, which through their normal metabolism convert  $\text{NO}_3\text{N}$  to simple gases that are vented into the air. The water is then released into a river, stream, or ocean.

This use for methanol is not expected to grow appreciably, since it is desirable only in certain areas and there are more proven conventional methods for nitrogen removal. Politics also play a large part in building methanol dinitrification plants, at least in the United States.

Nitrogen removal from wastewater is usually associated with inland areas or more pristine locations, for example Florida. Sewage plants located adjacent to large bodies of water, such as oceans or gulfs, can use these resources to discharge wastewater. Other areas may require additional processing before wastewater can be discharged into rivers and streams. It all depends on the environmental considerations and regulations of a given location. In the United States, funding is available for a methanol dinitrification plant from the Environmental Protection Agency, provided the applicant can prove this is the preferred route in view of location, water quality required, and so on, but capital costs are considerably higher than for more traditional plants.

Methanol is more expensive for nitrogen removal than other carbon substrates, such as brewery wastes, molasses, and whey. In many cases it is preferred, however, because it can be utilized to extinction. There are only a few such plants in the United States and perhaps as many more in the rest of the world.

## 9.7

### Summary

#### 9.7.1

#### North America

In the past, Mexico was in a more or less break-even situation. Its methanol production and consumption were rather closely balanced, but occasional export availability found homes in the United States and Western Europe. In 1986, Mexico liberalized its international trade policy and allowed consumers to ne-





gotiate and transact imports directly rather than through the state oil company, PEMEX. More recently, the federal government of Mexico has moved further toward decentralization and even to privatization of many companies, but not the state oil company. This has encouraged Mexican imports of methanol. There had been past plans to utilize local natural and associated gas to feed one or two new large methanol plants, but it is our opinion these projects have been postponed indefinitely. However, besides the plans for two large world-scale methanol plants, there are very preliminary plans of a more definite nature to build a world-scale MTBE plant in Mexico that will include a small methanol plant to supply the alcohol feedstock.

Canadian methanol production, especially the two plants located in the Province of Alberta, were in very serious financial difficulty in the mid-1980s. The cost of the feedstock natural gas was not considered a value comparable to that of other remote-area producers, and it is expensive to ship this methanol to deep-water export facilities, located in Kitimat and Vancouver in British Columbia. Attempts were made to ship methanol via a products pipeline from Edmonton, Alberta to Vancouver and also via a liquefied petroleum gas pipeline from Edmonton to Chicago and Windsor, Ontario, but these tests proved only marginally successful and the methanol that was received was off-specification and suitable basically only for fuel uses. The two Alberta methanol producers, Novacor and Celanese Canada, reduced their total costs by renegotiating feedstock gas contracts and shipping rates both to Canadian export ports and directly to the United States.

Both Canada and the United States agreed to a free-trade pact that took effect January 1, 1989. Under the terms of the agreement, U.S. import duty on methanol was to be phased out over a period of 5 years. However, the duty phase-out was accelerated by mutual agreement, and as of April 1990, all U.S. import duty on Canadian methanol and MTBE has been eliminated; the reverse is also true for Canadian imports of methanol and MTBE from the United States.

Great promise is seen for methanol producers in the western provinces of Canada in supplying their product to a wave of new MTBE facilities coming on-line in the West Coast states of the United States, a very natural market for Canadian producers. Also, a new world-scale dehydro MTBE plant came on-line in Edmonton, Alberta in 1992 that finds lucrative markets on the U.S. West Coast.

According to official statistics [2], Canada is the largest methanol exporters to the United States, and this is expected to continue well into the future. Methanol arrives in the United States via tanker ships (even in the U.S. Gulf) and also by direct railcar shipment across the border into the upper Midwest. In fact, Canadian methanol producers have been supplying the United States very reli-

ably for about 15 years, and they are considered a first line of supply, comparable to U.S. producers.

Formaldehyde production in North America is expected to be rather flat in the near term but then increase eventually. Actually, although formaldehyde production in the United States has not been very strong during the past 2 years, and in fact even registered some declines, Canadian formaldehyde production is rather strong. With the North American Freed Trade Agreement, Canadian formaldehyde is finding new markets in the northern portion of the United States, which is pushing back U.S. formaldehyde production. As usual, diemthyl terephthalate (DMT) production is expected to remain rather stable in this region of the world. After some debottlenecking, acetic acid production in the United States should realize some increase, providing additional methanol demand, but it will also level off. The big winner, as usual, is MTBE. According to Table, methanol demand for MTBE production during the 4 year study period should expand by a total of about 209%, which equates to almost 33% per year. Indeed, this could prove to be somewhat on the optimistic side, but a number of announced and even not yet announced MTBE plants are scheduled to begin construction either this year or next that will be on-stream during the study period. All in all, for North America we anticipate methanol demand increasing by about 4.8 million t between 1991 and 1995, for a total increase of 86% or about 17% per year. This increase will quite obviously be led by MTBE production.

### 9.7.2

#### Western Europe

The Western European petrochemical market is a true dichotomy. In some ways petrochemicals are homogeneous, and in other ways they are not.

In the methanol sector, there is much intraregional trading, especially among European Community member nations. Geography and topography have much to do with this, along with past plant shutdowns in some countries, such as Spain, France, and Italy. The focal point for methanol trading is Germany, the largest producer, importer, and consumer. Some methanol consumers, especially those in Italy, France, and Spain, are not pleased with the fact that the German methanol market has a very strong influence on pricing in their markets. This goes back to previous times, when most methanol supplies in the Mediterranean area originated in Rotterdam and a differential was required for the additional freight. Only Libya, with a methanol plant that started up in the late 1970s, was able to supply the Mediterranean directly without going through Rotterdam, but for some reason the differential continued for awhile. There is at present large methanol storage at and around Lavera in southern France, and questions arise why methanol prices for delivery to this port should be above Rotterdam prices, which are in turn influenced by the West German market. On the other hand, some

of the ports in the Mediterranean and also the Iberian Peninsula are small and simply cannot handle large ships. These destinations justify higher freight rates over Rotterdam because of the parcel sizes involved and higher port costs and diversions, for example.

Some of the outlying Western European nations, such as the Nordic countries, Spain, and Italy, rely mostly on methanol imports from so-called deep-sea sources. These sources are as close as Libya and the former Eastern Bloc and as far away as Saudi Arabia and New Zealand. There are preliminary plans to build a world-scale methanol plant on the western coast of Norway that would be supplied by associated gas from a new offshore crude oil platform. Since the platform has not yet been built, nor has the delivery system to the mainland, we do not anticipate this plant to come on-stream until sometime in the middle to later part of this decade. The preliminary plans call for the associated gas to be delivered to the shoreline commingled with the crude oil and separated at that point. The plans also include a world-scale MTBE plant to utilize part of this methanol production. The only other new development in methanol production in Western Europe is that, since the reunification of Germany, the Leuna Werke plant in former East Germany (now eastern Germany) falls under Western European methanol-producing capability.

Methanol demand for formaldehyde in Western Europe has been very soft, and it is not expected to reverse in the near term. However, should the rebuilding of the eastern countries occur anytime soon, it is very possible that formaldehyde production could increase proportionately. A new acetic acid plant came on-line at the BP facility at Hull in the United Kingdom a few years ago. Although it had some initial problems, we understand it has been running quite well. MTBE production in Western Europe is expected to level out very soon. There probably are still a few refineries that could utilize the C<sub>4</sub>s from their FCC units to produce MTBE, but we do not anticipate any new MTBE production from dehydro or other sources, with the exception of the new MTBE plant scheduled for the west coast of Norway that could come on-line in 1996/1997, outside our study period. Although we indicate approximately 50,000 t/year of methanol demand yearly in the study period for gasoline blending, we anticipate that this will occur only in Germany. There is a very good chance that with the expected increase in methanol pricing and the stability of crude oil and gasoline values, methanol-gasoline blending could disappear entirely in Western Europe during the study period. There are some small gasoline distribution companies, especially in northern Germany, that continue to blend in small amounts of methanol with cosolvents to keep their gasoline distribution systems clean and dry, but this might not be so attractive if and when methanol is no longer economical.

According to our study, methanol demand for formaldehyde production is expected to increase by a total of about 4.7% during the study period, or more than 1% per year. This could be above what some others would forecast, but as mentioned previously, we are counting on increased formaldehyde demand for eastern Germany and eastern countries and also because the current recession should be over by the end of 1993. DMT expansion is expected to remain rather stable as usual. It can be seen from Table that an additional 200,000 t/ year of methanol is expected to be required in 1995 for the production of acetic acid. This takes into account the new Hoechst facility that has been announced for Germany. We will probably have a better idea on this late 1993 or early 1994. Methanol demand for MTBE production is expected to grow at approximately 10% in total for the 4 year study period. Some new methyl methacrylate production will be coming on-line in Western Europe, but this increased methanol demand is not very significant. All told, during the 4 year study period between 1991 and 1995, methanol demand is expected to increase in Western Europe by 10 million ton, or 10% in total. Western Europe's dependence on imported methanol is expected to increase in the 4 year study period from approximately 2.5 to 3.0 million ton, an increase of 20%, and in 1995 total Western European methanol demand will be based on imports of about 53%. We are rather conservative in our estimates of expanded methanol demand in Western Europe during the next 4 years. The global recession has been debilitating, and for the most part methanol demand in Western Europe has reached maturity. As mentioned previously, however, there is tremendous promise for Western European industry in general to rebuild the economies of their eastern neighbors. This will not occur until very firm guarantees can be given to Western industries to invest in the rebuilding efforts with a minimum of risk.

### 9.7.3

#### Far East and Asia

This region of the world is generally widespread geographically, and methanol shipments and deliveries can range from full ships of 40,000 ton or more to small bulk tanker deliveries of about 700 ton, to very remote islands where formaldehyde plants might be located. These logistics provide a challenge to the transportation industry.

Economic and political problems persist in both countries as the Philippines, whereas other countries, such as Malaysia and Indonesia, are striving to find their place in the sun. Along these lines, there are current plans to develop a "golden triangle" between Jahore Baru, Singapore and the island of Batam in Indonesia, where a number of refineries and petrochemical facilities are planned to be built within the next 10 years. This development would provide tremen-

dous opportunities for the refining and petrochemical industries and could definitely include expanded MTBE production. We do not show these possibilities in Table simply because they are only preliminary plans at this time.

On the other hand, some countries, such as South Korea and Taiwan, are becoming more competitive against Japan and they are increasing their share of many export markets. Therefore, the economy of some Far Eastern countries could experience continued growth in the future, but at the expense of Japan, who provided the original role model of increasing exports. In fact, the global recession has also hit the Far East and Asia. Currently, Japanese economic growth is rather stagnant and may even develop into negative numbers. The economies of South Korea, Taiwan, Singapore, and Hong Kong are growing more slowly than they did during the past 10 years, but they are still ahead of most other countries in the world. This region of the world is a true economic dichotomy.

Some years ago, Japan made a very realistic appraisal of the future of its methanol industry. Decisions were made to close the more expensive producing plants and to import methanol from various worldwide sources at cheaper prices. These decisions were inspired by the industry for the good of the industry, and the previous producers still market imported methanol through their existing networks. The result is a more competitive methanol position that, it is hoped, carries over to the derivatives and export markets.

South Korea and Taiwan have followed Japan's lead in this approach, shutting down expensive methanol production and importing at less expensive world prices. One exception is the 66,000 ton per year plant commissioned in Taiwan in 1986 that uses refinery off-gas as a feedstock that might otherwise be flared. But we understand the plant might now be shutdown permanently, making Taiwan a 100% methanol importer.

In the far East, new methanol production came on-stream in the 1980s in New Zealand, Malaysia, Indonesia, and Burma. One fact is rather apparent: with the methanol commitments of some Japanese companies either in a direct equity position or as firm purchases with other global producers, all this new production will not be able to find a home in the Far East for many years to come, and exports out of the region are necessary.

Methanol demand in the Far East is expected to grow only in line with chemical uses in this decade. Consumption for formaldehyde is and will continue to be the largest single outlet. Formaldehyde production is expected to grow at moderate to healthy levels in Japan, Korea, Taiwan, and Pakistan. Consumption of methanol for DMT and acetic acid should grow with new capacity scheduled, and consumption for all other chemicals is expected to grow at gross national product levels.

So far very little interest appears in the methanol fuels area in the Far East, except with some thought given to blending into gasoline in some countries, such as India. However, this might not be a good idea without extreme proper care and monitoring, since it is almost impossible simply to blend methanol into gasoline without proper cosolvents. The problem is even more critical with older cars because the methanol and alcohols can "clean out" fuel systems in automobiles and dump the deposits in carburetors. There are some plans to develop methanol fuel cell technology in Japan, especially for some more remote islands for power generation. This would eliminate the need to deliver fuel and residual oil to these locations. A public utility in the southern part of Japan is currently experimenting with methanol as a fuel. We understand this experiment will last about 18 months and will consume about 2000 ton methanol per month. The test should be over in the third quarter of 1993. In 1992, MTBE was approved for use in Japan, but only at a blend of 7% and only in premium gasoline. Some Japanese refineries are now in the process of installing MTBE plants in their facilities to use C4 from the FCC units.

Practically all the older and less efficient methanol plants have already been shut down in the Far East. We therefore believe the rationalization process has just about reached maximum proportions in the Far East, with the exception of one small operating unit in Japan. There is always the possibility, of course, that rapidly expanding consumption of methanol or the termination of purchase contracts for methanol produced outside the region will reduce the surplus in the Far East, but we do not expect this to happen in the study period. What little is being planned in fuels or other new major potential methanol outlets will take a long time to reach reality and make a dent in the surplus.

Japan has had the most stable methanol market in the world, and there is one basic reason: Practically all the major methanol marketers were previous producers who have shut down plants but retained market share through imports. These markets are tightly controlled by only a handful of players, some of whom have an interest in the Japanese-Saudi Arabian consortium. The working relationship is one of mutual cooperation for the common good, an approach prevalent in the Far East but difficult or illegal to practice in other regions. However, competition for the Japanese market from outside sources has become quite strong recently and is expected to increase.

Formaldehyde production continues to remain relatively strong in the Far East and is expected to expand at about a total of 11% over the 4 year study period. Demand for formaldehyde products in Japan is somewhat strong, but there have been some environmental concerns because of the depletion of the rain forest in Malaysia and Indonesia to supply wood products for Japan. So far this has not become a major problem, but it could at some point in the future, thereby



reducing formaldehyde production in the region. We do not take this possibility into account at this time. DMT production in the region is expected to increase somewhat higher than originally anticipated. New acetic acid production has and will be coming on in a few locations, most notably in Korea and Japan, and assuring that production will be maximized, we calculate expanded methanol demand for acetic acid at above 100% in the region for the study period. As far as MTBE production is concerned, the only real production expansion possibilities we show in the study period are those in Malaysia, Japan, Korea, and Singapore. New methyl methacrylate production will be coming on-stream in the region, increasing methanol's demand for that outlet.

Methanol demand in the Far East and Asia is expected to increase at approximately 24% in total during the four year study period, or at more than 4% per year.

No new methanol-producing capability is expected to come on-line during the study period, unless Petrocorp in New Zealand decides eventually to add even more distillation and storage capability to "clean up" another 450,000 t/year of crude methanol into chemical grade. Otherwise, a number of new methanol plants are contemplated for such locations as Malaysia and Indonesia, but the principals are having difficulty in lining up financing. On the other side of the coin, we expect reduced methanol production throughout the Far East because of chronic production problems in Indonesia, Malaysia, Burma (Myanmar), and Taiwan. Therefore, the combination of increased methanol demand and less local production can only tend to make the Far East more dependent on methanol imports from other regions of the world.

#### 9.7.4

##### South America

According to our best estimation at the present time, the following are some methanol projects being considered for various countries in South America and the Caribbean area.

Under construction in Trinidad is another plant of 500,000 t/year in Point Lisas, which is adjacent to the site of the existing methanol plant and ammonia facility. This is the Caribbean Methanol Corp. project scheduled for completion in late 1993.

Natural gas is available on the northern and eastern shores of Trinidad that has not yet been commercially developed, and the owners are considering another methanol facility.

At least one other plant could be scheduled for Trinidad, making a total of three in project and one currently in operation. As far as we are aware there is sufficient gas in Trinidad, but much of it must be developed and brought onshore to feed any new large gas-consuming projects, including methanol.



In early 1991, Pequiven brought on-line a world-scale MTBE plant at San Jose, Venezuela. There are plans for a second MTBE plant and also for two methanol facilities. A 660,000 t/year methanol plant is currently under construction by Mitsubishi of Japan and Pequiven of Venezuela. This facility should begin production in 1994. Another methanol plant in the planning stage would be a joint facility between Pequiven and Ecofuel of Italy.

Petroquimica Austral continues to search for potential backers for a world-scale methanol plant proposed for the Tierra del Fuego region of Argentina, and Coastal of the United States is currently involved in discussions. This project has been active for quite a number of years, and various interested parties have reviewed it and eventually backed out.

As can be seen, there are ambitious plans to build methanol facilities in South America. Because of the difficulty in putting together financial packages and also the country risk involved in some of the locations, we doubt very much that all these plans will be developed.

The great impact on methanol demand in South America is the new requirement for blending into gasoline in Brazil. In 1989, Brazil started to import large quantities of methanol as a replacement for ethanol. The world sugar market became rather strong and Brazilian sugar growers prefer to concentrate on the global sugar market at higher returns rather than provide feedstock for fuel ethanol production. Since Brazil entered into this fuel alcohol program approximately 10 years ago, about 4 million cars in the country are based on fuel ethanol. Therefore, there was a very serious shortfall of automotive fuel in 1990. Last year, Brazil imported approximately 480,000 ton methanol for these automotive fuel purposes alone. Additional methanol was imported for the production of MTBE. During our study period we anticipated that Brazilian methanol imports for MTBE will continue according to traditional patterns, but we expect a decrease in imports for fuel purposes. As far as Brazilian fuel methanol imports are concerned, much depends on conditions at the time. Import licenses are issued only for 36 month periods, and the quantity allowed depends on how much ethyl alcohol is available from the sugar farmers and other factors as well. Brazil does not like to use hard currency for needless imports, although sugar imports provide additional hard currency for methanol imports. In any case, we anticipate that Brazilian fuel methanol imports will decline over the coming years.

New MTBE capacity is coming on-line in South America during our study period. We expect methanol demand in South America for all other uses to grow according to traditional patterns. It is very interesting to note that, when considering the increase in methanol demand for MTBE and the decrease in methanol demand for fuel blending in Brazil, during our study period there will be

a net decrease in methanol demand in South America by about 6%. During this period, new methanol production is expected to come on-stream in Trinidad and Venezuela, together with a debottleneck in Argentina, which will more than double methanol production capability in South America. At a production rate of 90% of nameplate, we anticipate that South America will have increasing quantities of methanol available for export during the study period, reaching almost 20 million ton in 1995. Primary markets for this product would be in North America and Western Europe.

### 9.7.5

#### Middle East and Africa

It is well known that this area of the world has large methanol feedstocks in the form of natural, associated, and refinery gas. It is therefore not surprising that about 2 million ton new methanol production capacity came on-stream between 1983 and 1985 in the Persian Gulf and North Africa. There is very little current methanol demand in this part of the world, and most of the production is exported. At the present time, methanol production in the Middle East and Africa is dominated by Saudi Arabia and Libya. The plant in Libya started operations in 1978 and was expanded in early 1985. In early 1992, the Japanese consortium completed construction on a second plant at the Ar-Razi facility at Al Jubail. In fact, there are some very preliminary plans to build a third methanol plant at Ar-Razi. In addition to the current methanol facilities in the Middle East, which includes the plant in Bahrain, we are aware of the following plans for other locations.

1. International Octanes and Fluor Daniel Canada, both of Calgary, Alberta, have plans to build a joint methanol-MTBE facility in Qatar. The methanol quantity would be 600,000/700,000 t/year and MTBE 500,000 t/year. These are preliminary plans only, and since this project has not progressed to the engineering stage we do not show it in Table.
2. ICI/Penspen of the United Kingdom are proceeding with plans for a world-scale methanol facility, also in Qatar, that would include an MTBE plant. This would be on-line in 1994, and we show this possibility in our study period.
3. Metallgesellschaft/Lürgi of Germany also have some very preliminary plans for a world-scale methanol plant in Qatar, but since they apparently have not progressed very far, we do not show them in the study period.
4. Some French interests, led by Total, have been considering a combined methanol-MTBE facility in Algeria together with Sonatrach. Howev-

er, the recent political turmoil in that country and the resulting assassination of its president no doubt have delayed some of these plans.

5. Two of three 700,000 t/year methanol plants are also being considered for Nigeria.

It is very obvious that this region of the world has abundant supplies of methanol feedstocks. We are aware of some other plans in East Africa.

For the near term, methanol demand in the Middle East and Africa is expected to increase only in line with traditional uses. However, a large increase is expected in 1994 and 1995 when some of the new MTBE plants are scheduled to come on-line. This will cause Middle East and Africa methanol demand to more than double during the 4 year study period, but methanol export availability is expected to continue at relatively high levels.

The first world-scale MTBE plant came on-line in Saudi Arabia in 1988. It is a 500,000 t/year facility operated by SABIC. Neste Oy of Finland and Ecofuel of Italy are also involved in the project. To our knowledge, a number of additional MTBE plants are scheduled for the region, which by the mid-1990s could amount to a total additional MTBE production of over 3 million t/year, requiring more than 1 million t/year of methanol. We do not name specific projects here, but most of them would be second-generation field butane projects with nameplate capabilities of 700,000-800,000 t/year.

#### 9.7.6

##### Central and Eastern Europe

Without doubt, tremendous opportunities and challenges are available to Western and Far Eastern companies in Eastern Europe. For one thing, much of the industry is said to be highly polluting, very inefficient, and in extremely poor condition. In fact, in some cases, some of the facilities may have to be torn down completely and rebuilt. This provides opportunities not only for financial institutions and construction and engineering companies, for example, but also for the marketing organizations that would be required to supply product during the time of tearing down and rebuilding. The restructuring of the former Eastern Bloc countries will certainly be a revolution in all types of industries throughout the world.

As far as the methanol business is concerned, in the Central and East European countries, we do not expect any major changes, with a few exceptions. In fact, for the most part we believe that much of the information available from the former Comecon industries was rather optimistic in all areas that involved expansion. There are tremendous changes in the internal trade patterns of the Central and Eastern European countries in that they are attempting to reduce their own trade between the former Comecon countries and trying to maximize trade

with outside countries. Any internal trade is done for the most part on the basis of hard currency payments. This is a difficult transition for those former Comecon countries that relied on the former Soviet Union for supplies of natural resource feedstocks at subsidized or very low prices or on barter arrangements. They must now get up to speed with global economic factors and conditions, which is not easy to accomplish.

We do not doubt that methanol consumption in Central and Eastern Europe is at lower rates than that experienced previously. We show some slight increases in formaldehyde demand, most toward the end of the study period, when we anticipate increased economic activity. Some new MTBE facilities are due on-stream in 1993, or possibly 1994, which will also contribute to overall methanol demand growth. All in all, we anticipate methanol demand in Central and Eastern Europe to increase by only about 300,000 ton for a total of 14% for the entire study period.

On the supply side, we are aware of previous plans to construct new methanol-producing facilities in the former Soviet Union and also in Bulgaria. Until construction on these projects actually begins, however, we do not include them in our forecast. The reason is rather obvious: with the current political and economic turmoil in this global region, there is the real possibility that any production expansion plans could be delayed because of difficulty in arranging financing, among other problems.

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